SINTERING OF MANGANESE AND CHROMIUM CONTAINING LOW ALLOY STEELS

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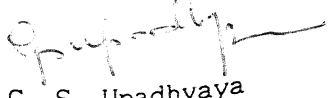
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This is to certify that the present work entitled **'SINTERING OF MANGANESE AND CHROMIUM CONTAINING LOW ALLOY STEELS'** has been carried out by Mr. Amitava Sinha under my supervision, and it has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENT

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ABSTRACT

The field of sintered low alloy steels is well established in P/M. Now ample stress has been given to develop sintered low alloy steels with cheap alloying elements like manganese and chromium. However, as these elements are having high oxygen affinity, sintering in dry hydrogen atmosphere had been adopted in the present investigation. High sintering temperatures (1250°C - 1350°C) were also used to get the favour of oxidation-reduction kinetics at those temperatures. The concentration of alloying elements, such as, Mn, Cr and a combination of both are valid upto 2.0%, and their effects are studied on sintering of steels. Properties of sintered steels, like sintered density, sintered porosity, microhardness, compressive yield strength, matrix grain size were studied. The heat treatment response of these steels has also been reported in the present work.

CHAPTER I

LITERATURE REVIEW

I.1   INTRODUCTION

The mechanical engineering industries are steadily coming to a better understanding of potentialities of P/M. The main users of P/M components are the automotive, business machine and other mass producing industries, which require large number of small metal shapes in their products. The greatest advantages of P/M process are economic mass production of precision parts without loss of material, and high strength to weight ratio. Materials with mechanical properties far exceeding those of more conventional materials have been developed by using new alloying elements for iron based materials by improving heat treatments, by using improved powders and by achieving higher densities. Not only can high strength be obtained but also high level of ductility and toughness in P/M parts are available.

I.2   Properties Required for Structural Parts

The field of low alloyed sintered steels is well established in P/M. With the attainment of better mechanical properties in sintered steels through higher density and alloying, the possibility of using them for components subjected to cyclic loading has not been overlooked by engineers, and comprehensive fatigue data are gradually being obtained. However, mainly expensive and relatively rare metals were used as alloying elements and the principal possibilities that we have for strengthening in steel technology are not fully used so far in P/M. Now considerable interest is attached to the study of sintered low alloyed steels, since important avenues of development in powder metallurgy would be opened up if it were

possible to obtain, at a low cost, P/M parts having mechanical properties comparable to those of conventional cast, wrought and forged steels.

The strengthening effect of a large number of alloying elements on sintered steel has been known for many years; e.g., nickel, molybdenum, manganese give strength and ductility. Since dimensional accuracy is of prime concern for the fabricators of sintered parts, the efforts put into increasing the strength of the material automatically create a dilemma, because above a certain strength level, the parts can not be sized. There are two possible solutions to the problem — one is to sinter the parts to a moderate strength, then size them and finally heat-treat them to the desired high strength. There is one snag with this method and that is the dimensional change upon heat treatment, which may throw the parts out of size very easily. The other possibility is to maintain such a precise control over the whole process that the parts come out of the sintering furnace with the desired tolerance and strength.

The control of furnace atmosphere has also been a significant problem and this has prevented the development of ferrous based alloys along with the conventional pattern for cast and wrought materials. In particular, elements that are readily oxidised can not be accurately controlled in commercially available equipment. Consequently carbon, the principal alloying addition in conventional cast and wrought ferrous alloys, has not been fully exploited in case of sintering. Other elements that would be valuable additions such as chromium, manganese, titanium are either readily oxidised or form nitrides in the atmosphere of commercial furnace. However, nickel, copper and molybdenum can be utilised in almost any reducing or neutral sintering atmosphere without oxidation problem.

Producers of sintered low alloy steel P/M parts often use heat treatment operations to improve the quality of their products. Such applications call for a material with an evenly distributed carbon content. A complete thorough hardening is usually followed by a tempering operation. Numerous data on the hardenability and transformation characteristics of wrought steels have been assembled over the last few decades. At first glance it may appear surprising that very little information exists on the heat treatment characteristics of sintered steels. To some degree this may be explained by the fact that powder metallurgists have adopted an already well established heat treatment technology and have used equipment and methods that have long been used for wrought steels. This, however, leads to certain pitfalls because the choice of alloying elements for sintered steels is influenced by entirely different factors than those which determine the composition of solid steels. Another possible reason for the lack of pertinent heat treatment data is the particular difficulty in acquiring such data owing to the porosity of the material. The existence of voids adds to the inaccuracy of hardness measurement and makes it difficult to control the carbon content at the surface of the material with sufficient accuracy. Therefore, such well known and widely used methods, such as Jominy test, are inadequate for the testing of sintered materials.

I.3   Selection Criteria for Alloying Elements and
           Associated Problems

Except for extremely thin parts, and very rapid heat treatment equipment, it is necessary to introduce additional alloying elements in order to enhance the hardenability of the material. The number of alloying elements that may be used in

sintered materials is rather limited. One must keep in mind that each kilogram of green compacts presents a surface of roughly 1000 m^2 to the atmosphere, which means that any thermodynamically unstable metal or compound is exposed to the deteriorating influence of the atmosphere to a much higher degree than in the case with solid material. For this reason, metals nobler than iron, such as copper, nickel, and molybdenum, were the first to be used extensively in ferrous powder metallurgy. Unfortunately, these elements are expensive in comparison with the most common alloying elements in low alloy steels — manganese and chromium. A number of authors have, however, shown that it is possible to base sintered steels on manganese and chromium, provided that certain precautions are taken to avoid oxidation during sintering.

The influence of various alloying elements on the hardenability of solid low alloy steels is shown in Figure 1.1 [1]. In the diagram, the hardenability is given in terms of a multiplying factor, a term introduced by Grossman which describes the influence of adding a quantity of the alloying element in question on the depth of hardening. It is evident from the curves that such elements are boron, molybdenum, chromium and manganese, which have a strong influence on the hardenability, whereas the effect of copper, nickel and silicon, is considerably weaker.

The choice of an alloying element is governed not only by its ability to raise the hardenability of the material and by its resistance to oxidation, but also by the possibility of achieving an even distribution throughout the structure of the sintered steel. For a discussion on this question, it is useful to consider first the various methods of introducing the alloying elements.

It has been a common practice in conventional
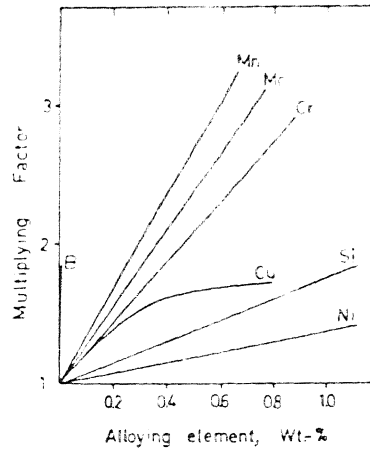
Figure 1.1 The Effect Of Various Alloying Additions On Hardenability According To Metal Handbook [1]

Figure 1.2 The Ei:ect Of Various Alloying Additions On The Strength Of Iron According To Lacy And Gensamer [1]

press-sinter powder metal application to achieve alloying by mixing or blending elemental powders to desired composition. By this method the compacted parts attain a high density because the elemental powders, especially the unalloyed iron powder, have a high compressibility. The alloying or more precisely partial alloying is achieved by diffusion during high temperature sintering operation. The actual degree of alloying will be related to the diffusivity of various elements at the sintering conditions and the powder surface conditions that may affect the initial absorption. It is not always practicable to allow enough time for the complete interdiffusion of the alloying element. A typical example of this is the use of nickel in mixes with iron. After sintering for one hour at 1100 - 1200°C (1375 - 1475 K) the structure shows evidence of inhomogeneity due to low diffusivity of nickel in iron in this temperature range.

Another means is to use a powder, each particle of which has the desired average composition of the alloy. Such powders are made by the atomization of molten steel. An obvious advantage with such powder is that homogenization during sintering is unnecessary. The alloying elements raise the strength of the individual powder particle, which means that they generally do not have as high compressibility as powder mixes. The selection of alloying elements for these powders may thus be based on the hardenability effect in relation to the solid solution hardening of the powder particles, i.e., loss of compressibility caused by the introduction of alloying element. Figure 1.2 shows the solid solution strengthening of pure iron by different alloying elements. A comparison between figures 1.1 and 1.2 shows that elements, such as molybdenum and manganese, are considerably more favourable than, for instance, copper and silicon.

If the ingradients in a powder mixture are bonded to each other by a thermal treatment, the product is converted into a partially prealloyed powder. This makes it possible to use very fine alloy ingradients which help to enhance the interdiffusion during sintering and thereby increase the degree of homogeneity of the sintered material. Partially prealloyed powders have the same compressibility as the powder mixtures, because the bulk of the powder particles are virtually unaffected by the alloying elements.

Table I.1 shows for some elements of interest, the melting point, the Grossman factor at a concentration of 1 wt% and the diffusivity in austenite at 1000°C related to self diffusivity of iron at the same temperature [1,2]. As a rough guide, the table also shows the free energy of oxidation for one mole of oxygen at 1000°C. It can also be noticed that with respect to 'cost of hardenability' point of view, manganese and chromium are the leading candidates — both have favourable diffusivities, although their oxygen affinity is high. Among the elements with low oxygen affinity, nickel and cobalt have low diffusivity in austenite.

The strengthening of sintered low alloy steels can be achieved through densification, alloying and heat treatment [3].

Densification can be brought about either mechanically or chemically during sintering. Mechanical densification can be achieved by increasing the compaction pressure, by pressing followed by sintering and repressing, possibly followed by resintering or by the development of softer powders. Chemical densification during the sintering process is assisted by increasing the sintering temperature or by the use of pressure-assisted sintering, activated sintering, liquid phase

sintering or infiltration, or by exploiting α-γ phase transformation.

TABLE I.1

Some Major Data for Alloying Elememts in Steels [1,2]

Element	Melting point, °C	Grossman Factor at 1% Level	Diffusivity $[D_x^{(\gamma)}/D_{Fe}^{(\gamma)}]$ 1000°C	ΔG (oxide) kcal/mol oxygen
Mn	1243	4.5	2.5	−140
Cr	1845	3.1	5.0	−130
Mo	2600	3.7	5.0	−75
Si	1423	1.7	10.0	−162
Zn	419	—	3	−100
Cu	1083	1.7	1.0	−37
Co	1495	(~ 2)	0.5	−65
Ni	1455	1.3	0.5	−60

Alloying can be used to strengthen sintered steels by the formation of solid solution or by adding constituents or both. In the sintered condition the constituents of fully prealloyed sintered steels are fairly close to equilibrium, but those in sintered steels made from elemental or master alloy mixes, partially prealloyed powders or coated powders are far from it. Their composition, structures and distribution can be influenced by the sintering condition adopted.

Heat treatment can be used to strengthen sintered steels either through quench hardening and tempering treatment, or through precipitation hardening, if, for example, copper is present. Fully prealloyed steels can be heat treated in a manner analogous to wrought steels. However, owing to their extreme

heterogeneity, both chemical and structural, steels made from elemental mixes, are susceptible to strutural modification in both the sintering and the heat treatment processes, which offers a unique method of manipulating the structures to produce the desired sets of properties.

Systematic studies on the grain size of sintered low alloy steels have not been made, but it is generally found that they have a considerably smaller grain size than most wrought steels and consequently one usually has to add more alloying elements to the sintered steels than corresponding wrought materials to achieve a certain specified hardenability. The small grain size has a beneficial effect on the strength of the material.

I.4   P/M Processing of Steels Containing Alloying Elements and Their Properties

I.4.1   Chromium containing sintered low alloy steels

The possibility to utilise elements with high oxygen affinity in sintered steels depends on whether they will maintain their metallic form during sintering or react with gases in the atmosphere and form insoluble compounds such as oxides. As described by Tenzelius et al. [4] the alloying elements can either be prevented from oxidation by sintering in an atmosphere which either is reducing relative to the metal/metal oxide system or has an oxygen content sufficiently low to cause oxidation of a minor part of the alloying elements only.

Harrison et al. [5] have reported that sintered low alloy steels having compositions including upto 1.5% chromium gave very poor mechanical properties and required high sintering temperatures. Their study showed that the furnace atmosphere was insufficiently reducing to prevent the formation of chromium

oxide during sintering. Vacuum sintering of chromium bearing alloys gave better results, but even these were not sufficiently promising to warrant further work, particularly in view of higher processing cost involved.

An exception to this behaviour was encountered when using a nickel coated chromium powder to make such addition, when the outer layer of nickel served to protect the chromium from oxidation during sintering.

As reported by Upadhyaya and Tewari [6], in carbon free iron, chromium is not a good solid solution hardener and, in fact, an iron - 3% chromium alloy is softer than unalloyed iron. In medium carbon alloys chromium retards the transformation of austenite to pearlite to such an extent that an addition of 2% chromium results in the formation of bainitic structure at relatively slow cooling rates. With low additives the pearlite formed is very fine, resulting in an increase in strength of the material.

Greetham et al. [7] in their study of low alloy sintered steels containing chromium have reported that the strength increases with increasing chromium content (upto 1% chromium), while the ductility falls. They used a series of powder mixtures containing 0.85% carbon with, 0, 0.5, 1.0, 2.0, 3.5 and 5.0 wt% chromium. The chromium was added in the form of low carbon ferro chromium alloy containing 71% chromium. The mixed powders were pressed to a green density of 6.8 gm/cc and sintered for one hour at 1300°C in vacuum.

Muller et al. [8] tried to develop high strength iron based alloys by using transition metal carbides. They selected carbides, as these have good solubility in iron, combined with high carbon content to achieve, after sintering, homogeneous and carbon rich alloy.

Tengzelius, Blände and Wastenson [4] prepared powder compacts made up of mixes of iron powder, finely ground iron-chromium and graphite; these were sintered in two different ways — (1) Belt furnace, 1120°C, N_2 + 5% H_2 + 1% CH_4, dew point -15°C, and

(2) Pusher furnace, 1250°C, N_2 + 5% H_2, in covered boxes.

The oxygen content bonded to chromium was very low and almost independent of sintering process as can be seen in Table I.2. The distribution of chromium, Q-value (explanation is given in the table) [10], is, however, much better in the material sintered at the higher temperature.

TABLE I.2

Oxygen Content Bonded with Chromium and

Distribution of Chromium [10]

Sintering Process	Oxygen Content Bonded to Cr (%)	Distribution of Cr, Q value*
1. Belt Furnace, 1120°C N_2 + 5% H_2 + 1% CH_4 dew point -15°C	0.12	300
2. Pusher Furnace, 1250°C N_2 + 5% H_2, covered box	0.08	20

* The Q-value [9] is a relative measurement of the distribution of an alloying element in a heterogeneous sintered steel. The method is based on a micro-probe linear analysis. The lower the Q-value, the better the distribution

The poor distribution of chromium in the steel sintered at 1120°C is due to the oxide layer formed around the alloying particles during sintering, which strongly retards the

diffusion of alloying element. By adding nickel to these chromium containing powders, a completely different and improved distribution of chromium is reached after sintering.

The strength of chromium bearing steel decreases when sintered in a nitrogen containing atmosphere, which can be explained by the formation of chromium nitrides. By analysing the content of nitrogen bonded as nitrides it was proved by Tengzelius et al., that chromium forms nitrides when sintered at $1120^{\circ}C$ in nitrogen containing atmospheres. Tengzelius et al. [4] had also reported the strength level obtained and dimensional change occured during sintering. They observed by adding a small amount of copper to the Fe-Cr-C material, the variation of dimensional change with combined carbon can be decreased. Dimensional precision and tensile strength above 700 N/mm^2 are reached with a high temperature sintered steel from powder with the composition Fe + 0.5% Cu + 1.5%t Cr + 0.7% C.

Vityaz and Nasybulin [11] reported during sintering of Fe-Cr-C steels produced from mixtures of powders, with different chemical compositions, homogenization takes place. The degree of uniformity can be evaluated from the standard deviation of histograms of alloying element concentration distributions. Such histograms were obtained by modelling the diffusion processes in sintering and from experimental data. The theoretical assumptions have been shown to give agreement with the experimental results. Mechanical properties such as ultimate tensile strength, elongation, reduction in area, hardness and impact behaviour are shown to improve gradually with sintering and homogenization.

I.4.2   Manganese Containing Sintered Low Alloy Steels

The beneficial effects of manganese in steel has

long been recognised. However, the use of manganese in sintered steel has been very limited, mostly because powder metallurgists have feared its relatively high affinity of oxygen.

Tests at Hoganas have shown, however, that when properly processed manganese containing powder is mixed with graphite, compacted and sintered under conditions that the carbon content of the material is kept at a constant level, most of the manganese dissolves in the iron and escapes oxidation [6]. Since manganese makes compacts to swell slightly during sintering, it is desirable to add small amount of nickel to the alloy in order to achieve dimensional stability. The distribution of manganese is also improved by the presence of nickel.

In carbon bearing steels, manganese depresses both the transformation temperature range and the eutectoid carbon concentration and, in consequence, any pearlite that is produced is very fine. Manganese, like nickel, can be used to stabilise austenite.

Among the various methods for alloying such cheap elements, through ferromanganese or sigma phase route, one through the addition of complex transition metal carbides has attracted much attention. Because of their high oxygen affinity, the small powder particles of these alloying elements are quickly covered with oxides, when exposed in air. These oxide layers form diffusion barriers during sintering and thereby present uniform homogenization of the alloy. The oxidation can be reduced or even prevented if the elements are prealloyed with other elements which are less sensitive to oxidation, or if compounds are used which are more resistant to oxidation. Ferromanganese and ferrochromium have been used and showed good results. As carbon is an indispensible alloying element in steels, carbides offer themselves as alloying additives [11].

Greetham et al. [7] in their study, used manganese in the form ferroalloy containing 75% manganese , which was added to a 0.85% carbon alloy in the proportion of 0.5, 1.0, 1.5 and 2.0 wt%. The mixed products were pressed to a green density of 6.8% - 6.99 gm/cc and sintered at 1300°C for one hour in vacuum. An addition of 0.5% manganese increased the tensile strength of the material significantly, but the strength did not increase further with increasing manganese concentration. The ductility of the specimens fell progressively with increasing manganese concentration.

In early seventies, work on manganese steels for P/M forging, Cook [9] showed the possibility of developing manganese and manganese-molybdenum steels having good hardenability and mechanical properties along with lower cost for powder forming applications.

Figure 1.3 shows the low carbon section of Mn-Fe-C (approximately 75% manganese) equilibrium diagram [13,14]. It can be seen that the eutectic of this ferroalloy system forms at 1095°C with a 3.8% carbon content. With the increase in carbon in the manganese liquid, carbides of the β - Mn_3C type form with the lower temperature of the liquid phase formation. Under these conditions with a 4 - 6.5% carbon content in the ferromanganese, the liquid phase is formed at less than 1100°C. This indicates that the liquid phase sintering of iron powder compacts with high carbon ferromanganese addition occurs already at 1100°C.

Zapf et al. [15] did extensive study on the role of carbon addition on sintering behaviour of Fe-Mn alloys. Their results (figure 1.4) show the influence of carbon upto 1.4% on the mechanical properties of single and double pressed Fe-2%Mn alloy. The optimum carbon content for both techniques was 0.6 -
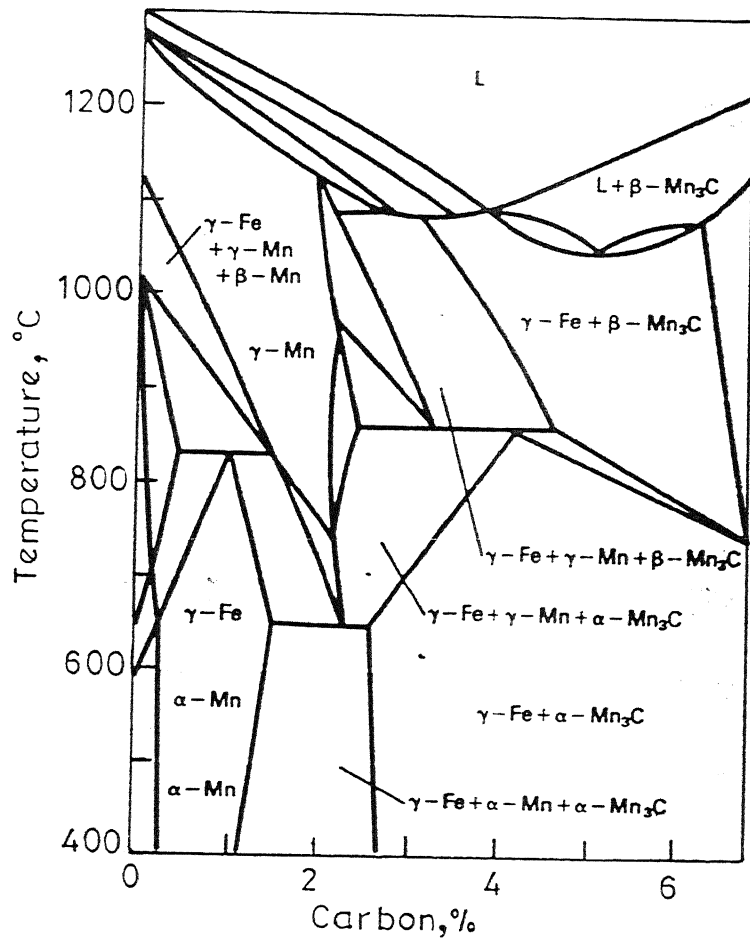
Figure 1.3   Section Through The Equilibrium Diagram Of The
Ternary Mn-Fe-C [12,13]
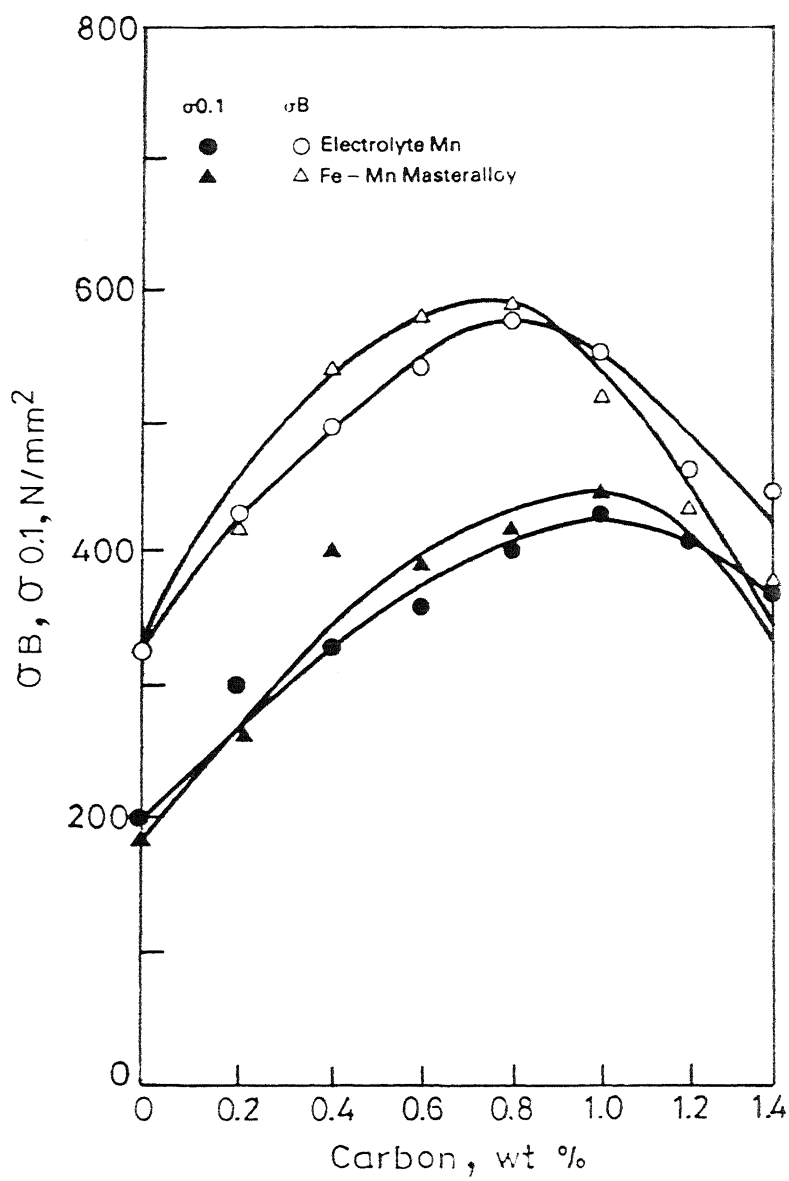
Figure 1.4   Effect Of Carbon Content On Strength Of Single
Pressed Fe-2%Mn Alloy [14]

0.8%. Tensile strength for single pressed alloy was nearly 600 N/mm^2 with a yield strength of 450 N/mm^2. The ultimate tensile strength of the double pressed alloys was 650 N/mm^2 and yield strength 500N/mm^2 (figure 1.5). The influence of carbon on the mechanical properties of alloys with greater than 2% manganese was very small.

Salak [12] investigated the effect of two types of iron powders (Hametag and atomized, particle size < 0.16mm) on the properties of sintered manganese steels with addition of manganese upto 5.5% in the form of high carbon ferromanganese (72.6 - 75% manganese, 5.5 - 7.75% carbon). The sintering was carried at 1120°C for three hours in dissociated ammonia. The use of Hametag iron powder, which had a fine grained recrystallized microstructure, gave better mechanical properties than atomized powder. It was proposed that manganese sublimates during sintering and its vapour condenses mainly on the fine particle surfaces and open porosity, thus contributing in the material transport. The strength deterioration of Hametag based steels after repressing and sintering were caused by two factors : (i) lower annealing temperature, necessitating a much cleaner atmosphere, and (ii) lowering of porosity level and consequently of manganese condensation.

For the preparation of P/M steels alloyed with manganese, air atomized iron powder (Hametag) with recrystallized annealed fine grain structure have been used [16]. The manganese was added in the form of 2.5 - 5.5% carbon ferromanganese. These compacts pressed at 589 MPa were sintered at 1120°C, forged and heat treated. The manganese steels, as forged and as heat treated showed considerably high properties when Hametag iron powder was used. Single pressing and sintering yielded ultimate tensile strength of 890 MPa in manganese steels, whereas heat treatment
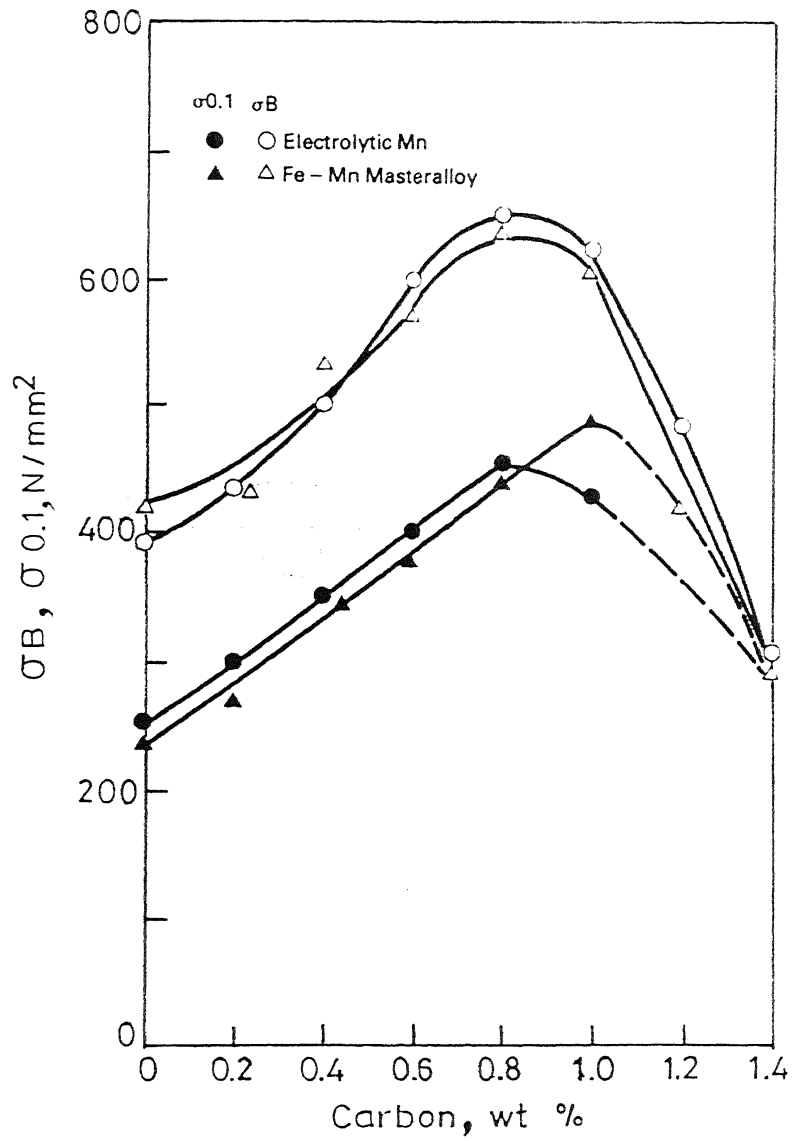
Figure 1.5   Effect Of Carbon Content On Strength Of Double
Pressed Fe-2%Mn Alloy [14]

yielded that of 1000 MPa. This indicates a way to increase the strength of P/M steels without increasing alloying addition.

Navara [17] studied the alloying of two types of iron powder with extremely different grain size, but similar particle size, with manganese during sintering. Manganese was added as low carbon (1% C, 75 - 80% Mn, 1% Si) and high carbon (5 - 7% C, 75 - 80% Mn, 1% Si) ferromanganese respectively. The author also confirmed the gaseous phase transport of manganese and established that the concurrent alloying in the solid state proceeds by grain boundary diffusion together with induced grain boundary migration. The degree of alloying, depended on the particle size of the iron powder, and not on its grain size, as significant grain growth occured before the actual sintering temperature was reached. According to the author the rate of evaporation of manganese far exceeds the rate of its oxidation in hydrogen (pure or diluted by inert gas) with a dew point around -20°C. This fact thus considerably mitigates the stringent requirement for a -55°C dew point, set by purely thermodynamic consideration.

Kaufman [18]has been a pioneer in introducing manganese in steels, such that alloying occurs by fusion of one component of the admixture. He used two master alloys, one a high carbon ferromanganese (Union Carbide made) and the other containing 8.5% manganese (Quebec Metal Powders). The compositions of this powder are given in table I.3. It was observed that melting occured below 1120°C for both master alloys. The Quebec Metal, being a hypoeutectic composition, melts eutectically to form a mixture of eutectic liquid with manganese rich austenite. Mechanical properties were sensitive to time and temperature for all the mixes.

TABLE I.3

Composition of Mn Containing Master Alloy [17]

Chemical Analysis (%)	Union Carbide	QMP
Fe	12.55	84.1
Mn	75.60	8.5
C	6.72	4.1
P	0.20	0.03
S	0.005	0.01
Si	0.53	0.09

Smith [19] used a high carbon ferromanganese (10% Mn, and 5% C) addition in water atomized state and having -325 mesh size (< 45 μm). Ford Motor Co. also developed a proprietary process for coating carburized ferroalloy particles with copper to limit the carbon loss prior to reaching sintering temperature. The transverse rupture test bars were sintered in hydrogen with a small amount of methane to maintain the carbon potential of 0.8 - 0.9% in temperature range of 1120 - 1200°C. All the compacts underwent a small amount of growth during sintering, which could be divided into two stages. At low temperature it grew about 0.2 - 0.3%, while at higher temperature it grew about 0.2% in the ten minutes sintering period, but it exhibited virtually no growth in the 30 minutes sintering period. The optical microstructures reveal that the ferromanganese particles had very limited attachment to the surrounding matrix. Another observation was that no liquid appears to have been formed around the ferromanganese particles. The change in the microstructure of the ferromanganese particles after sintering at 1175°C indicated increased distribution of manganese. The carbon loss occuring

during sintering seems to be the reason for the appearance of thin pore surface around ferromanganese particles. As the ferromanganese contains 3.5% O_2 mainly because it was obtained after water atomization, the reduction of surface oxide consumed carbon and thus left a pore space surrounding the particle. The copper coating thus had no effect in preventing carbon in present case.

I.4.3   Sintered Low Alloy Steels Containing Manganese and Chromium

The reaction of chromium and manganese with various sintering atmosphereshas been the subject of many investigators. Oxidation can be overcome by using powders with low contents of these elements, viz., prealloyed powders. Material made from powders containing different types of master alloys with high contents of elements such as chromium and manganese can and with correctly chosen composition, reach tensile strength values above 700 MPa after sintering at high temperatures (around 1250°C) or at lower temperature in combination with the use of atmosphere with very low oxygen potential.

Tengzelius et al. [21] discussed the possibility of using Fe-Cr-Mn-C material for high strength applications. Special attention has been given to dimensional change during sintering, as this property to such a great extent decides whether or not precision parts can be made economically by the P/M process. Because it is difficult to control the combined carbon content of the sintered material within narrow limits, such as ±0.5% C, the effect of variation of combined carbon on the dimensional change also has to be minimised.

The possibility to utilise chromium and manganese

as alloying elements in sintered steels depends on whether they will maintain their elemental form during sintering or react with gases in the atmosphere and form insoluble compounds such as oxides.

The findings regarding reactions during nitrogen atmosphere sintering between chromium and nitrogen corresponds well with the nitrogen equilibrium diagram. This diagram also shows that manganese will not form nitrides under the same conditions. Manganese, however, has a higher affinity to oxygen than chromium which at commonly used sintering temperatures makes it even more important to prevent oxygen from contaminating the sintering atmosphere. Test results have shown that sintering of compacts made of powder mixes with ferromanganese at $1120^{\circ}C$ in N_2- based atmosphere with a dew point of $-15^{\circ}C$ results in a sintered steel with a good distribution of manganese.

In spite of high degree of homogeneity, tensile strength of these manganese containing materials was almost equal to that of unalloyed Fe-C materials. However, by sintering this material at $1250^{\circ}C$ a marked improvement of mechanical properties was achieved. Therefore, in order to fully utilise these oxidation prone alloying elements in sintered steels, high temperature must be used.

Sintering is generally carried out at temperatures around $1120^{\circ}C$. However, higher temperatures have the advantage of a more favourable oxidation reduction equilibria when such inexpensive but oxidation prone alloying elements as chromium and manganese are used. Another advantage is the possibility to reduce the sintering time and still reach a good distribution of the alloying elements.

At the higher sintering temperature, as the kinetics for reduction of oxides are more favourable, the impact

properties are improved [20]. As the oxygen content is reduced the impact properties are improved.

Zapf et al. [15] studied the effect of carbon on the sintered Fe-2Mn-2Cr alloy. Mechanical properties are shown in figure 1.6, which shows that 0.6% C is the optimum content.

Motooka et al. [22] studied in detail the effect of oxygen content on the mechanical propoerties of manganese-chromium sintered steel. In order to study this effect, conventional grade atomized Fe-Mn alloy powder (>0.3% O_2) and newly developed low oxygen content powders (<0.2% O_2) were used. To study the effect of oxygen content after sintering on the mechanical properties, different sintering atmospheres, such as vacuum, hydrogen and cracked ammonia, were used. Table I.4 shows the oxygen content of specimens after sintering (1250°C, 30 minutes). The results showed that the mechanical property, especially impact toughness, strongly depended on the oxygen content, improving as the oxygen content decreased (figure 1.7). They also showed that the effect of carbon content on the mechanical properties of manganese-chromium sintered steels, which confirms that the impact property is improved as carbon content decreases.

TABLE I.4

Oxygen Content of Sintered Compacts [22]

Sintering Atmosphere	Oxygen Content, ppm
Cracked NH_3 gas	900 - 1200
H_2 gas	600 - 800
Vacuum	300 - 600
Vacuum in controlled atmosphere	90 - 300
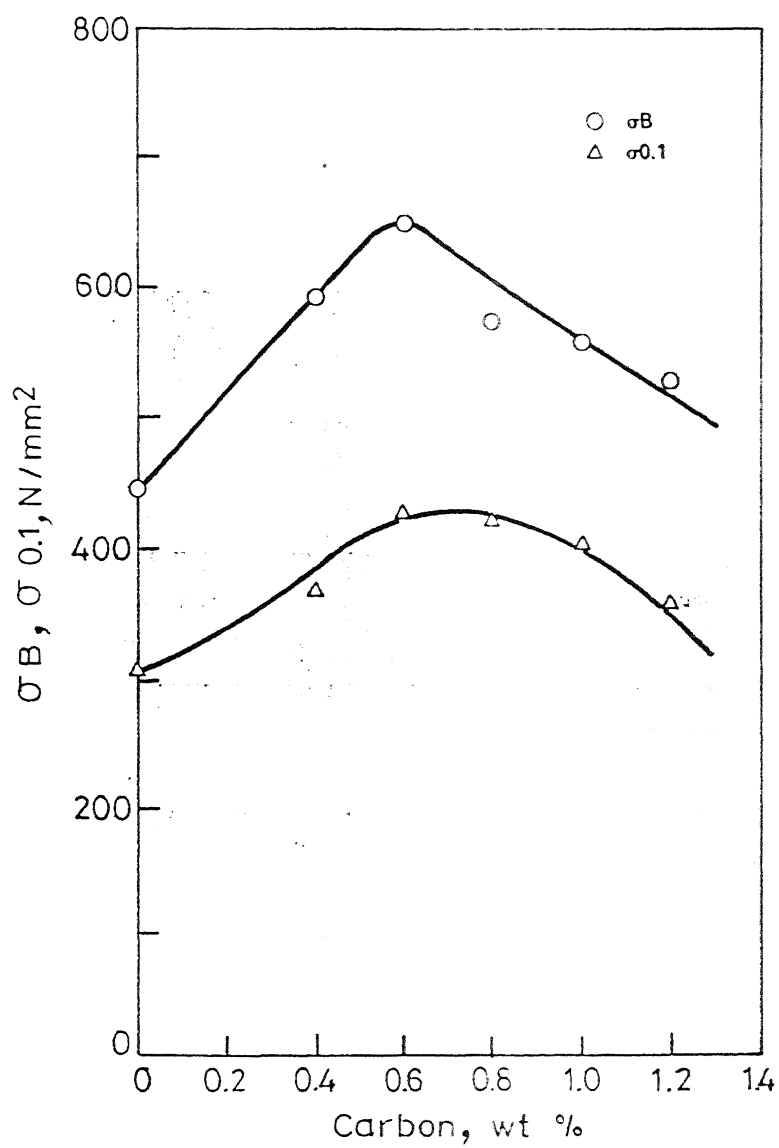
Figure 1.6 Effect Of Carbon Content On Strength Of Single Pressed Fe-2%Mn-2%Cr Alloy [14]
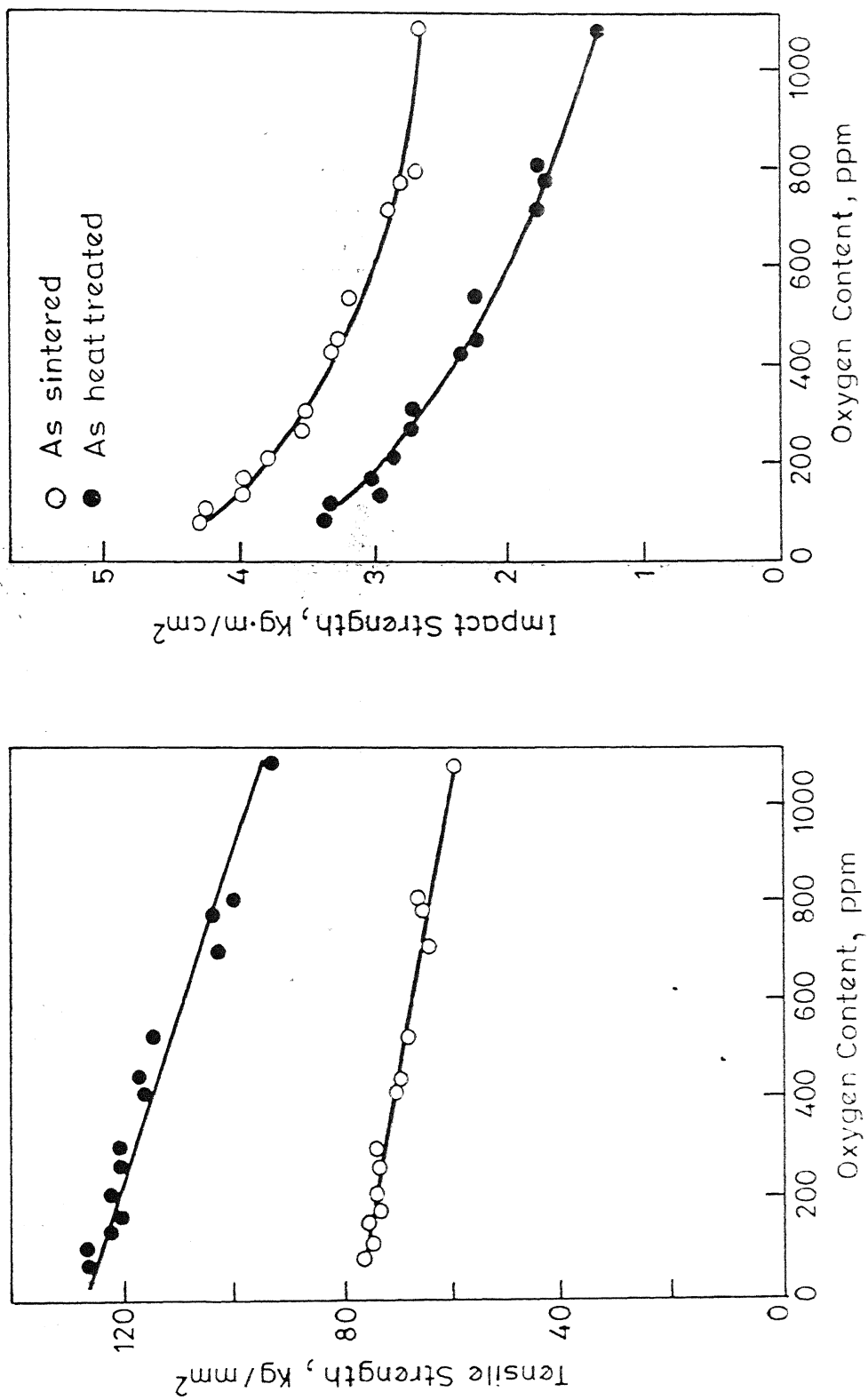
Figure 1.7 Effect Of Oxygen Content After Sintering
Mechanical Properties Of Mn-Cr Sintered Steel [22]

As described earlier, the reduction of the easily oxidisable metals like manganese and chromium can omly be carried out at temperatures attainable in industrial mesh belt furnaces (1150°C) or by applying vacuum at lower temperatures. A recent work [23] has shown that high temperature sintering can be economically feasible and can be competitive to mesh belt furnace operative at lower temperatures. Tengzelius et al. [4] on this assumption studied sintering behaviour of Fe-1Cr-1Mn-C steels with varying carbon contents, when sintered at 1250°C in N_2 + 5% H_2 atmosphere for 30 minutes using closed boxes.

Lindskog and Grek [24] performed several studies with manganese-chromium steels by sintering at temperatures upto 1300°C in dissociated ammonia or argon atmospheres. They showed that the impact strength and percent reduction of area in tensile test were determined primarily by the oxygen content of the alloy and by the heat treatment. Lower oxygen contents gave higher impact results (upto 68 J with R_c 24-27) and higher percent reduction of area (upto 40%), while quenched and tempered steels gave higher impact values than normalized steels. They also showed that the hardenability of an alloy was directly related to its oxygen content -- lower oxygen contents yielded higher hardenability.

I.5   Scope of the Present Investigation

On the basis of literature review, one can easily notice the importance of studying the sintering behaviour of manganese-chromium steels. It has been reported in literature that usual atmosphere prevailing in industrial furnace is not sufficient to prevent oxidation of manganese and chromium. It is, thus, recommended to use vacuum, cracked ammonia or hydrogen with some inert gas during sintering of manganese-chromium steels.

Among various methods of introducing manganese and chromium in low alloy P/M steels, one in which these elements are introduced as ferroalloy additives, is gaining more and more importance. The advantages of liquid phase sintering, particularly in high carbon ferroalloy, can be explored. This would give better densification and distribution of alloying element in steels.

The effect of sintering on phase transformation response of sintered low alloy steels containing various carbon contents would be worthwhile to study.

As manganese and chromium are known to have better contribution towards hardenability of steels, these steels containing manganese and chromium can further be heat treated to improve the sintered properties.

The present work is aimed at studying the high temperature (1250°C - 1350°C) sintering behaviour of manganese-chromium steels through ferroalloy additives.

CHAPTER II

EXPERIMENTAL PROCEDURES

The detailed experimental procedures carried out in the present investigation are presented in this chapter.

II.1 Powder Characteristics

The characteristics of the powders selected for the present investigation are as follows.

II.1.1 Iron Powder

High compressibility sponge iron powder, grade NC 100.24 was obtained from HOGANAS AB, Sweden, was selected as base material.

Characteristics of this powder are :

Carbon content	: 0.01%
SiO_2	: 0.22%
H_2 loss	: 0.22%
Apparent density	: 2.4 Mg/m^3
Flow rate (Hall - Flow meter)	: 31 sec/50gm
Compressibility	: 6.4 Mg/m^3 at 420 MPa
Particle size	: +100 mesh ... 0.5% approx.
	-325 mesh ... 21.5% approx.

II.1.2 Ferro Alloy Powders

Ferrochrome and ferromanganese powders supplied by Ferroalloy Corporation (FACOR), India, were used as source of chromium and manganese respectively, in the P/M steels.

Below given are the compositions of those ferro-alloys :

Composition	Ferrochrome	Ferromanganese
Cr	63.8	—
Mn	—	73.48
C	0.05	7.10
Si	0.80	0.80
S	0.03	0.04
P	0.035	0.36
Fe	Balance	Balance
Flow rate (Hall - flowmeter)	42 sec/50 gm	46 sec/50 gm
Apparent density	3.08 Mg/m^3	3.96 Mg/m^3
Particle size	-325 mesh	-325 mesh

II.1.3   Graphite

The graphite used was natural one (99.9% pure) and had a particle size of -300 mesh.

II.2   Preparation of Powder Premixes

Three different sets of compositions were prepared by mixing different constituents for one hour using a manual mortar and pestle. First two sets of alloy steel powder premixes containing manganese or chromium (0 - 2%) were prepared by mixing 0.6% and 1.2% carbon respectively. Another set of alloy steel powder premixes were prepared with 1.2% C, such that the amount of manganese and chromium were equal in each premix.

The table 2.I gives data for the calculated

theoretical densities of various compositions (presuming the rule
of mixtures is valid).

Table 2.I

Theoretical Densities of Steels with Various Compositions

Carbon	Composition (mass%)	Theoretical density (gm/cc)
	Alloying Element	
	0	7.754
	0.5 Mn	7.751
	1.0 Mn	7.749
0.6	2.0 Mn	7.745
	0.5 Cr	7.750
	1.0 Cr	7.747
	2.0 Cr	7.739
	0	7.641
	0.5 Mn	7.639
	1.0 Mn	7.636
	2.0 Mn	7.632
1.2	0.5 Cr	7.637
	1.0 Cr	7.634
	2.0 Cr	7.627
	0.5 (Mn + Cr)	7.638
	1.0 (Mn + Cr)	7.635
	2.0 (Mn + Cr)	7.630

II.3 Compaction

From the powder premixes cylindrical green
pellets of 1.27×10^{-2} m diameter and approximately 0.6×10^{-2} m
height were prepared in a single acting, manually operated
hydraulic press. The pressure employed for preparing the pellets
was 675 ± 25 MPa. The die wall was lubricated with zinc stearate

prior to powder filling. Heights and diameters of green pellets were measured with vernier callipers (least count 0.002 cm) and from that the volume of each pellet was calculated. Their weights were found out by weighing in a Metler single pan automatic balance (least count 0.0001 gm). From the weights and volumes of the pellets, green densities were calculated.

II.4 Sintering

Furnace description : The furnace used was a resistance type, the heating elements being silicon carbide rods. The furnace tube was made of alumina and was of 5 cm diameter and 90 cm length. The furnace rating was 1.8 kVA. It had a constant temperature zone of 10 cm, and temperatures were controlled by an on-off type controller. The temperature of the furnace was measured by a platinum / platinum - 10% rhodium thermocouple. The heating rate of the furnace was controlled with the help of a dimmerstate voltage regulator which controlled the voltage across the heating elements.

Hydrogen was passed through the furnace tube in order to maintain a reducing atmosphere. The hydrogen was dried in a Lectro drier. Hydrogen being an explosive gas, the furnace was sealed with heat resistant silicon rubber (SILASTIC) in order to prevent hydrogen from coming into contact with atmosphere at elevated temperature.

All the specimens of different compositions were kept in the nimonic boat and were sintered under identical conditions for one hour at three different temperatures, viz., 1250°C, 1300°C and 1350°C. For every set of conditions three samples were prepared.

The heating and cooling rates were $6^{\circ}C$ /min and $9^{\circ}C$/min respectively and the temperature control was $\pm 5^{\circ}C$. After allowing the sintered specimens to be furnace cooled, linear and radial dimensions of the specimens were measured. The method used for measuring the sintered densities of the samples was same as in the case of green densities.

II.5 Heat Treatment

Austenitization was carried out in a vertical silicon carbide furnace. The samples were packed in cast iron chips to prevent the possible decarburization during heating. The heat treatment was carried out only on the samples (1.2% C) which were sintered at $1300^{\circ}C$. All the sintered steels were austenitized to $870^{\circ}C$ for 20 minutes and then quenched in water at room temperature. Microhardness of the quenched samples were measured with maximum load of 500 gm after grinding the specimens upto a depth of approximately 0.5 mm from the surface in the axial direction followed by usual polishing and etching. The tempering of the hardened steels was not carried out because of the presence of multiple phases, i.e., bainite and retained austenite apart from the martensite.

II.6 Microstructural Examination

For the metallography, sintered specimens were first manually polished on Lunn Major Polisher which are provided with emery papers of grades 1/0, 2/0, 3/0 and 4/0. Final polishing was done on a polishing cloth on a disk polishing machine using 0.3 μm alumina suspended in distilled water. The specimen were examined under optical microscope after etching

them with 2% nital and micro photographs were taken.

II.7   Property Measurement

II.7.1   Sintered Density

The sintered densities of all the samples were determined by measuring the dimensions and weights of the specimens after sintering.

II.7.2   Sintered Porosity

Sintered porosity was calculated using sintered density (II.7.1) and theoretical density (Table 2.I) as per following expression :

$$\% \text{ sintered porosity} = \left(1 - \frac{\text{sintered density}}{\text{theoretical density}}\right) \times 100$$

II.7.3   Vicker's Microhardness

Microhardness of sintered and quenched samples were determined with the help of 'Leitz Miniload 2' Vicker's microhardness tester. The loads used for measuring the microhardness of sintered and hardened samples were 15 gm and 500 gm respectively.

II.7.4   Grain Size Measurement

The grain size of sintered steels with alloying additions manganese or chromium, for carbon levels of 0.6% and 1.2% was measured. The method used for measuring grain size was described by Smith and Guttman []. Accordingly the following formulae were used :

$$S_V = 2 N_L \qquad\qquad 2.1$$

$$2 S_V = \frac{4 \pi (D/2)^2}{4/3 \pi (D/2)^3} \qquad 2.2$$

$$D = \frac{3}{S_V} = \frac{3}{2N_L} \qquad 2.3$$

where S_v = grain boundary per unit volume ;

N_L = mean number of intercepts of random test lines with the grain boundaries per unit length of est line ;

D = mean grain diameter.

Microphotographs of each steel sintered at three different temperatures were taken. Random test lines were drawn on the photomicrograph and N_L was counted. Using eq. 2.3, grain size was determined for each specimen.

II.7.5 Compressive Yield Strength

Compression test of all the sintered specimens has been carried out on 'Instron' universal testing machine. During compression tests, the cross head velocity was fixed at 0.2 mm/min. The load versus displacement curve was obtained and from that 0.2% offset stress values were calculated for all the sintered steels.

II.7.6 SEM Studies

EDAX analysis of some of the steels was carried out under scanning electron microscope with 1500X magnification. A representative field was selected and chemical analysis of three points on each steel was carried out to determine the distribution of alloying addition. These were in the grain interior away from the grain boundary and near the grain boundary respectively.

CHAPTER III

RESULTS

III.1 **0.6% C steels with Mn or Cr addition**

**III.1.1** Sintered Density / Porosity

Figures 3.1 (a,c) and 3.1 (b,d) show the variation of density and percentage porosity with increasing alloying addition of Mn or Cr containing steels respectively sintered at different temperatures. Measurements of porosities in the sintered compacts showed that the percentage porosities in manganese containing steels were less than in chromium containing ones.

III.1.2 Microhardness

Figures 3.1 (e) and 3.1 (f) show the variation of micro hardness with increasing manganese and chromium content for 0.6% C steels. It can be seen that the effect of alloying addition on micro hardness is different at different sintering temperatures. The hardness of sintered steels with increasing chromium content showed higher values after $1250^{\circ}C$ and $1300^{\circ}C$ sintering,but after $1350^{\circ}C$ sintering, the effect was reversed. In general, the hardness increases with increase in the amount of alloying element.

III.1.3 Compressive Yield Strength

Effects of increasing the amounts of manganese and chromium in 0.6% C steels can be seen in Figures 3.1 (g,h). It can be seen from the plots that the compressive strength (0.2% offset) of manganese steel is higher than the chromium
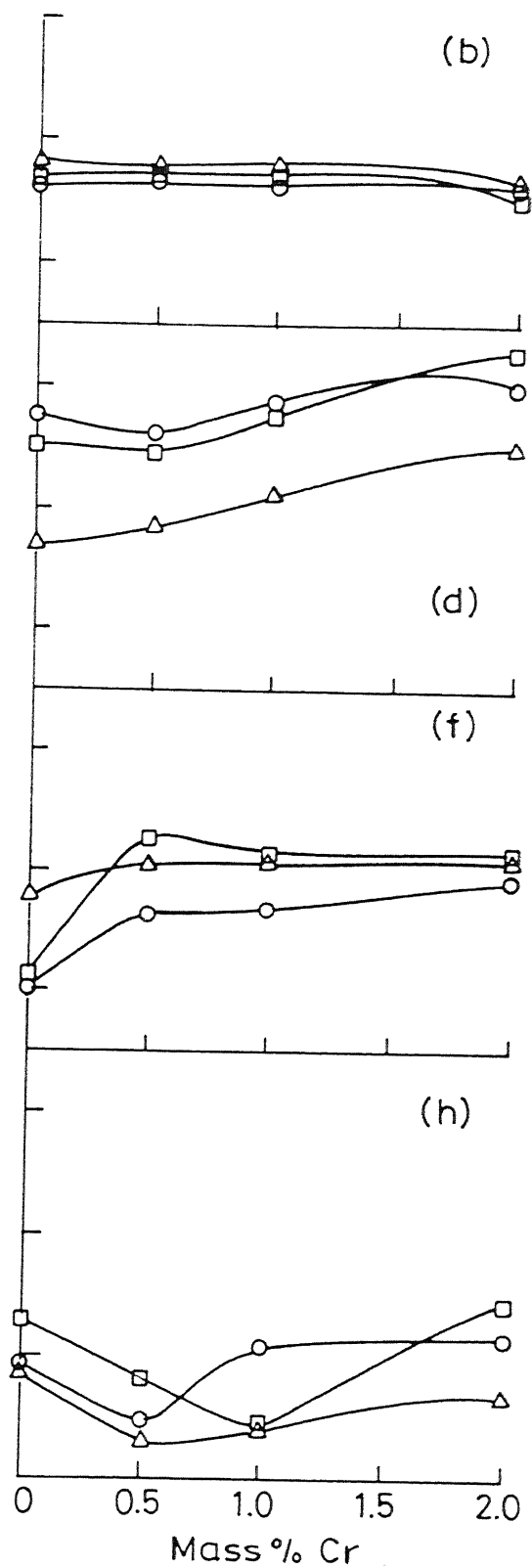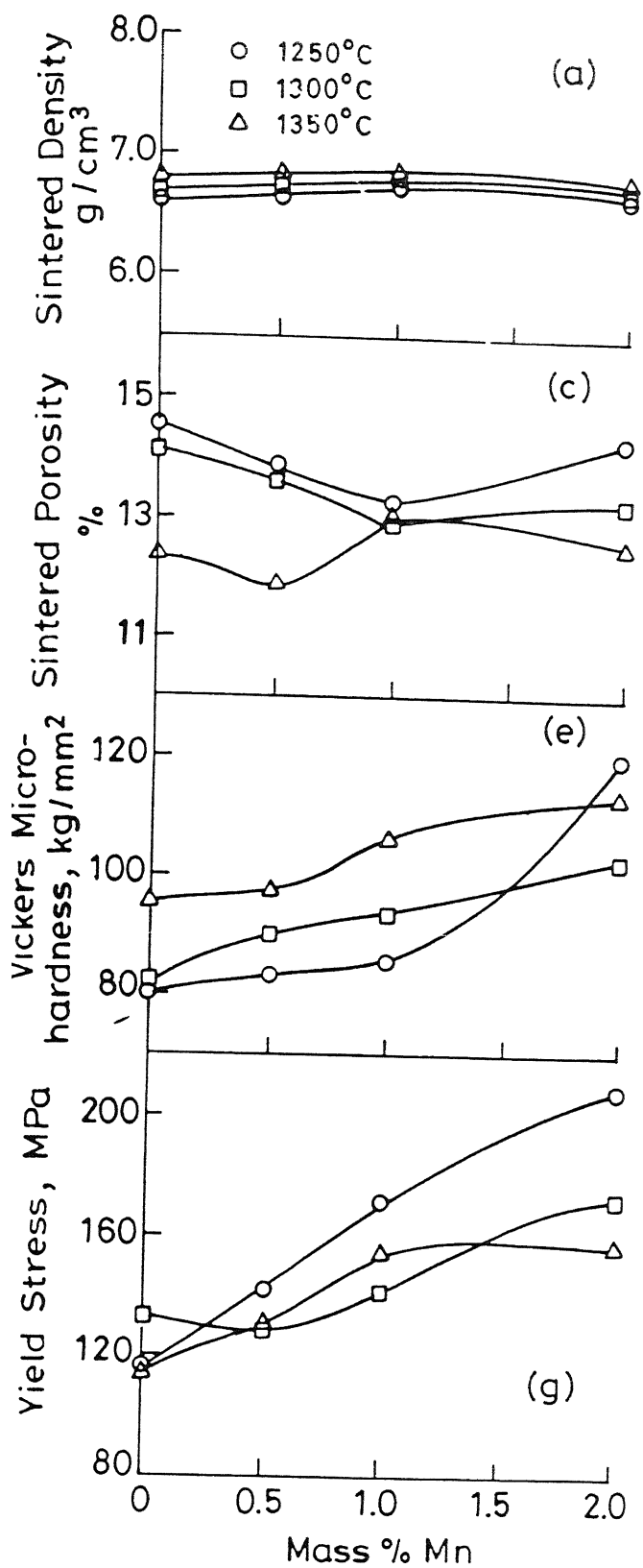
containing ones. In case of 0.6% C steels, similar to hardness variation, there was an appreciable increase in compressive yield strength for manganese containing steels with increase in alloying content. However, in case of chromium containing steels there was no significant change in strength with increasing alloying addition.

The effect of sintering temperature on compressive yield strength was found to be different from that on hardness variation, as an intermediate strength level at the highest sintering temperature (1350°C) was noticed.

III.1.4   Optical Metallography and Grain Size Variation

Figure 3.2 shows the micro-structure of 0.6%C steels with various manganese and chromium contents (0-2% wt) when sintered at 1350°C. The optical micro-structures revealed mainly ferrite grains along with pores.

The alloying addition had a significant effect on grain refinement. From the quantitative measurement of grain size, it was observed that the grain size, in general, decreased with increasing amount of alloying elements [Figure 3.3]. Furthermore, the extent to which the grain size was reduced, was more in case of manganese addition than chromium addition. This was true for all the sintering temperatures ranging from 1250° to 1350°C. It was also noticed that at any particular sintering temperature and amount of chromium or manganese , the grain size was coarser for chromium containing steels than for manganese ones.

III.1.5   SEM Studies
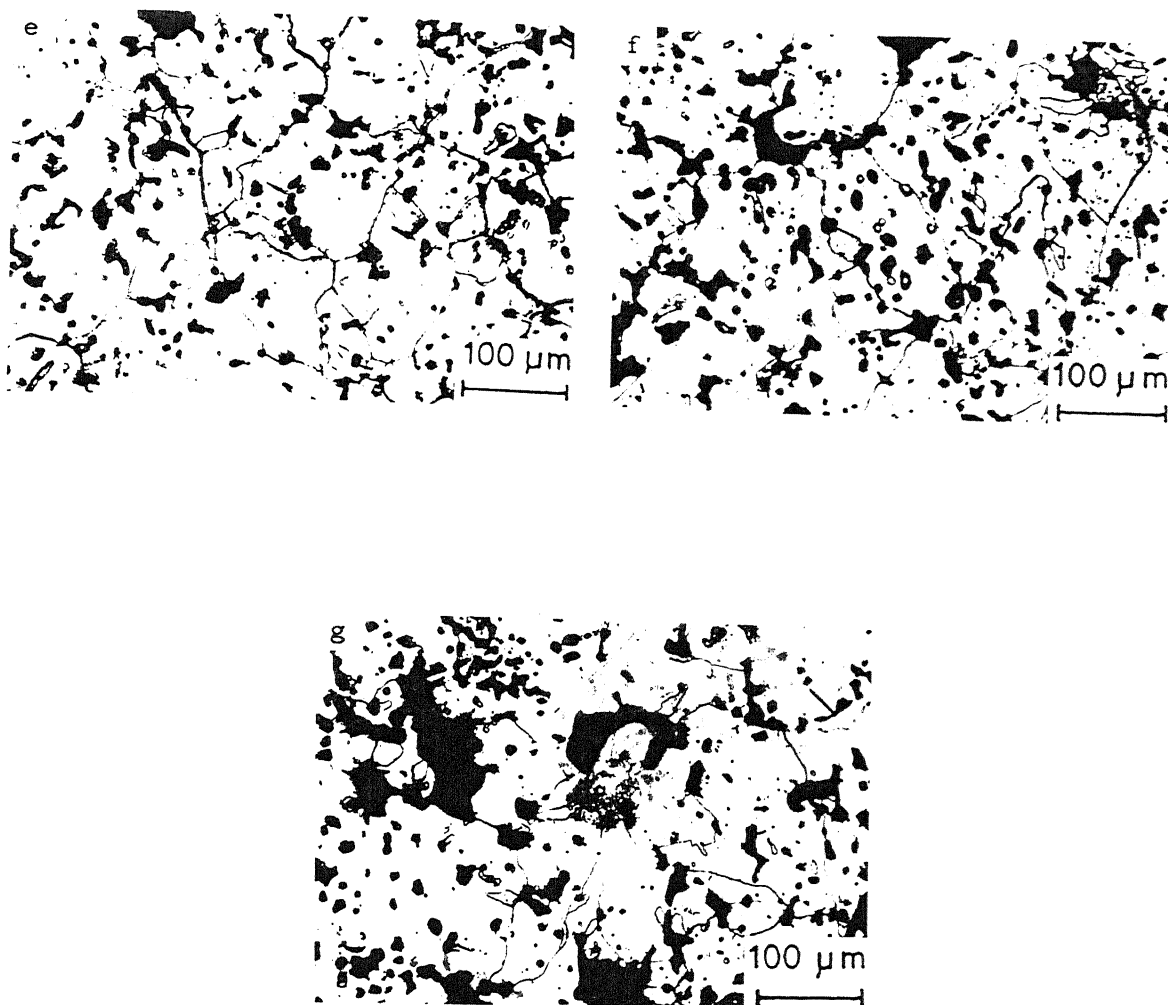
The chemical analysis (EDAX) carried out in
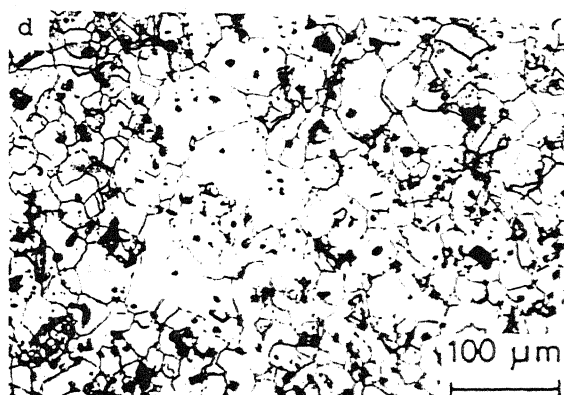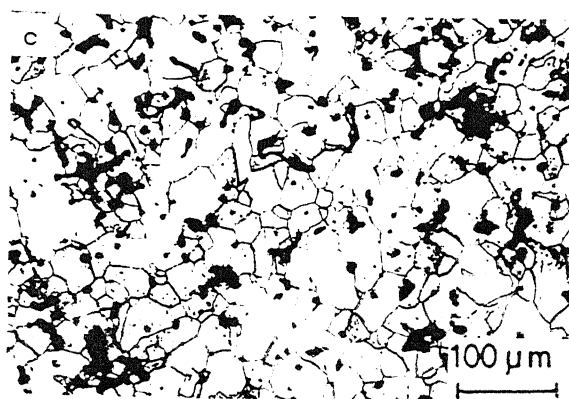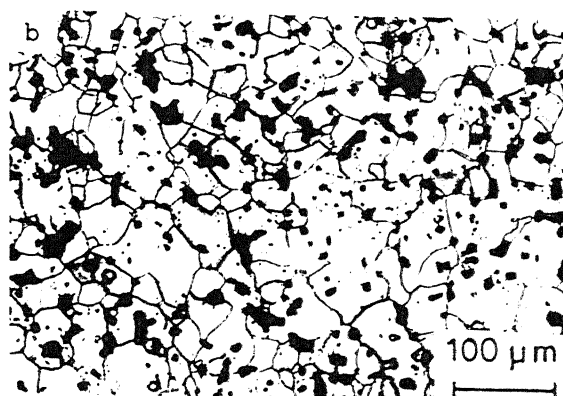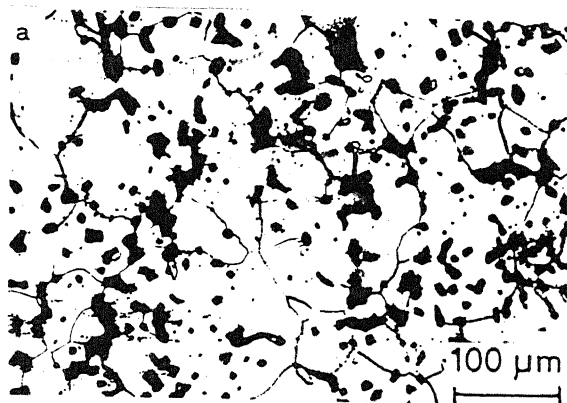
Figure 3.2   Microstructures Of Steels (0.6% C) Containing
0-2% Manganese Or Chromium (Sintered At 1350°C For One Hour In
Dry Hydrogen)
     (a)   0% alloying ; (b) 0.5% Mn ; (c) 1.0% Mn ; (d) 2.0% Mn
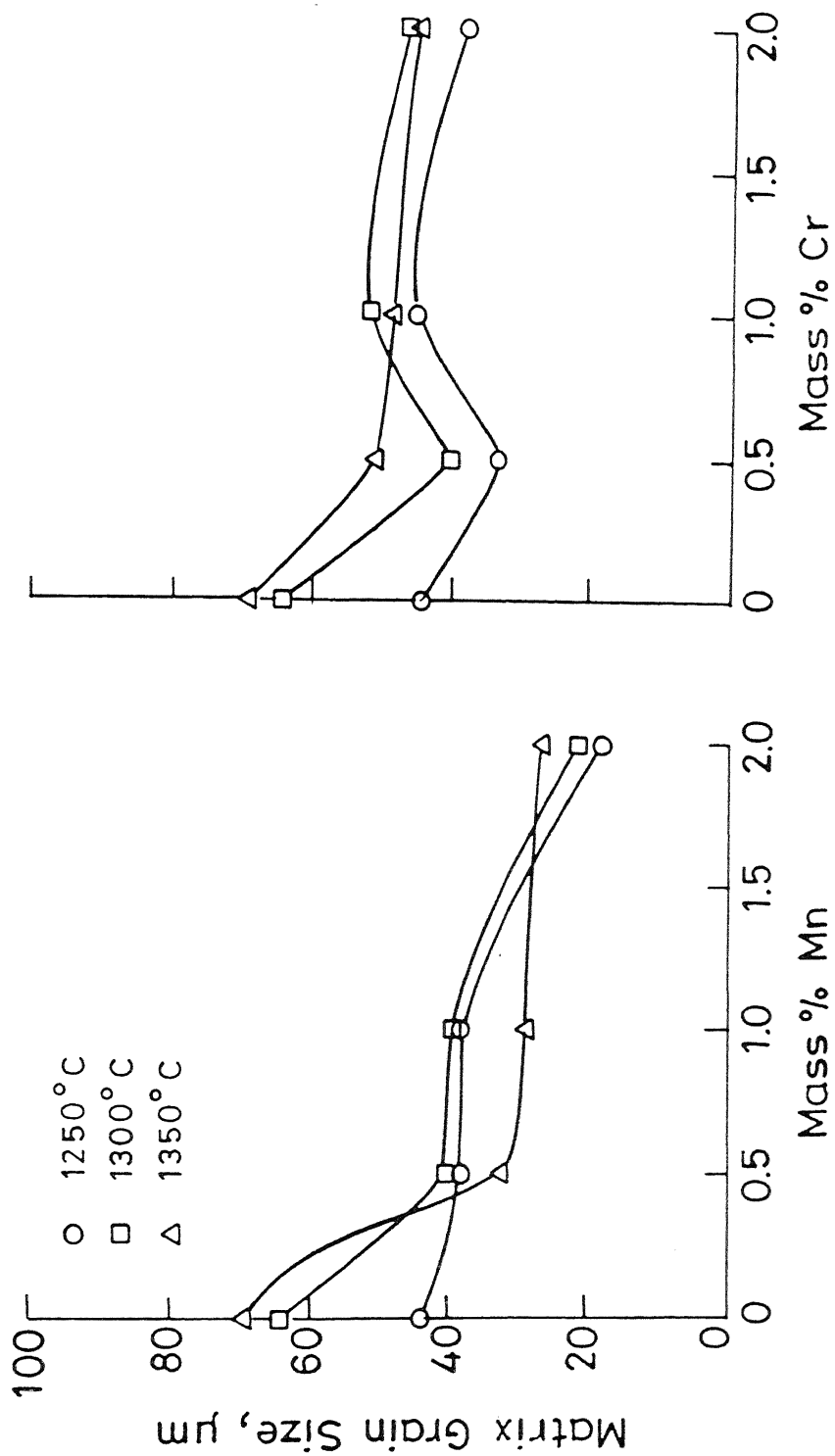   (e)   0.5% Cr ; (f) 1.0% Cr ; (g) 2.0% Cr

Figure 3.3   Matrix Grain Size Variation With Respect To
Manganese Or Chromium Content For Steels Containing 0.6% C
(Sintered at 1250°C – 1350°C For One Hour In Dry Hydrogen)

SEM revealed that the concentration of manganese increased uniformly as one proceeded from grain interior to grain boundary [Table III.1 (a)]. At elevated sintering temperature (1300°C), the amount of manganese dissolved in the matrix was lower than that of 1250°C sintering.

In case of chromium containing steels (0.6% C) it was noticed that the alloying element was distributed more uniformly than those in manganese containing ones. However, the amount of dissolved alloying addition was less than in the manganese steels [Table III.1 (a,b)].

SEM photographs of steels containing 1% alloying addition and sintered at 1300°C showed that chromium steel had more undissolved ferrochrome particles than in case of manganese steels[Figure 3.9].

III.2   1.2% C Steels with Mn or Cr addition

III.2.1   Sintered Density / Porosity

Like 0.6% C steels, in 1.2% C steels also there was not much variation of sintered density with increase in the alloying contents. Figures 3.4 (a,b) show highest sintered density of compacts sintered at 1350°C, for either types of steels.

In manganese steels, with increase in carbon content from 0.6% to 1.2% there was a general decrease in porosity [Figure 3.4 (c)]. However, such a feature was not observed in case of chromium steels [Figure 3.4 (d)].

III.2.2   Microhardness

The micro-hardness variations of 1.2% C steels, sintered at three different temperatures for either

TABLE III.1 (a)

EDAX Analysis of Manganese in 0.6% C Steels

Composition Temperature	Location in Photomicrograph	0.5% Mn Steel	1.0% Mn Steel	2.0% Mn Steel
1250°C	A	0.69	1.33	1.50
	B	0.73	1.51	1.58
	C	0.92	1.52	1.79
1300°C	A	0.27	0.48	1.13
	B	0.91	0.65	2.53
	C	0.95	0.56	2.60

A : Grain interior ;   B : Near grain boundary ; C : At grain boundary

TABLE III.1 (b)

EDAX Analysis of Chromium in 0.6% C Steels

Composition Temperature	Location in Photomicrograph	0.5% Cr Steel	1.0% Cr Steel	2.0% Cr Steel
1250°C	A	0.27	1.06	0.41
	B	0.26	0.54	0.46
	C	0.28	0.62	0.43
1300°C	A	0.22	0.26	2.59
	B	0.30	0.26	3.12
	C	0.31	0.63	3.71

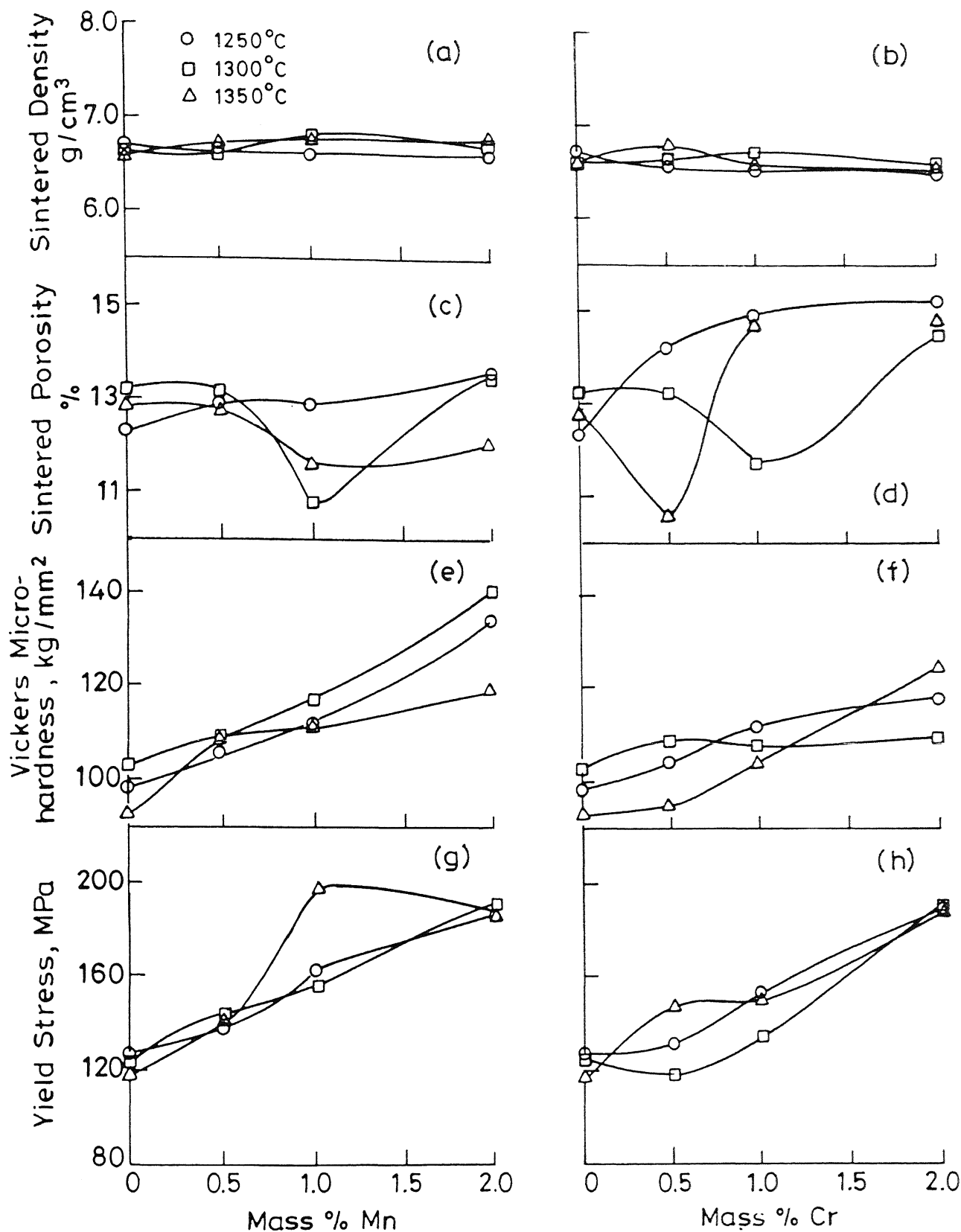A : Grain interior ;   B : Near grain boundary ; C : At grain boundary

Figure 3.4 Sintered Properties Variations With Respect To Manganese Or Chromium Content For Steels Containing 1.2% C

manganese or chromium additions are shown in Figures 3.4 (e) and
3.4 (f) respectively. It can be noticed that manganese containing
steels possess higher micro-hardness values than the chromium
containing steels.

The positive effect of increased carbon level on
micro-hardness is also evident.

III.2.3   Compressive Yield Strength

0.2% offset compressive yield strength values of
1.2% C steels with various manganese or chromium additions are
plotted in Figures 3.4 (a) and 3.4 (b) respectively. The nature
of variation was similar to 0.6% C steel for all alloying
additions. The chromium containing steels (1.2% C) exhibited
better strength than the corresponding steels containing 0.6%
carbon.

III.2.4   Optical Metallography and Grain Size Variation

Figure 3.5 shows micro-structures of 1.2% C
steels containing manganese or chromium ranging from 0-2 wt %.
The optical micro-structures show comparatively lower level of
porosity in 1.2% C steels than in 0.6% C steels. The grain size
variations in such steels sintered at 1300° and 1350°C showed
similar trends as in 0.6% C steels, with overall decrease in the
grain size. The effect of increased level of carbon content from
0.6 to 1.2% in lowering the grain size was more significant in
Cr-steels than in Mn-steels.

III.2.5   SEM Studies

Similar to 0.6% C steels, in 1.2% C steels with
ferro-manganese addition, the concentration gradient of manganese
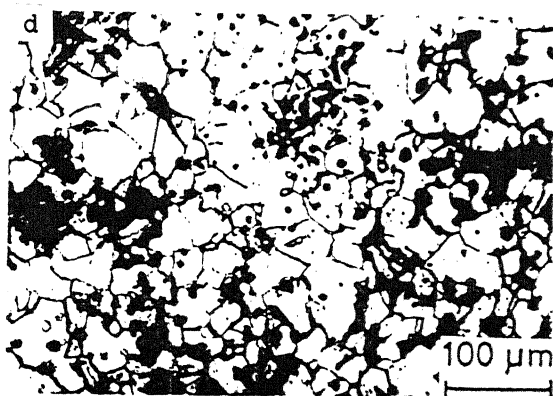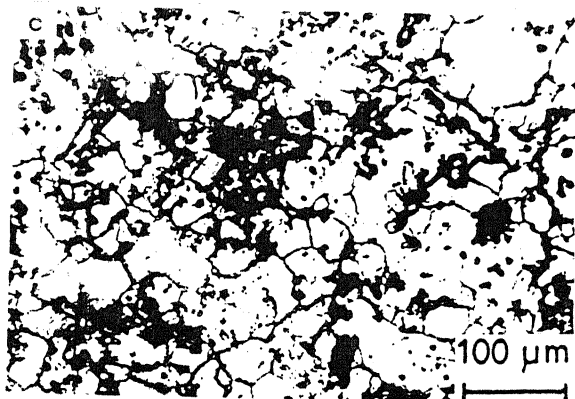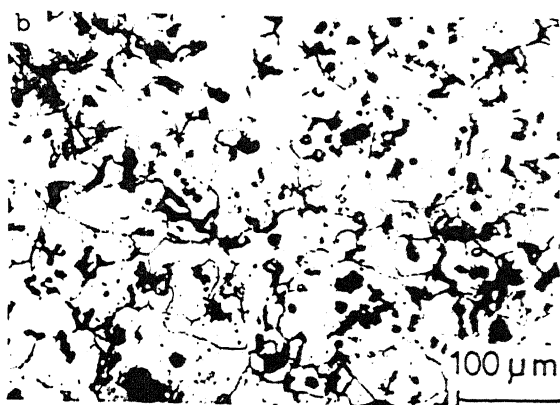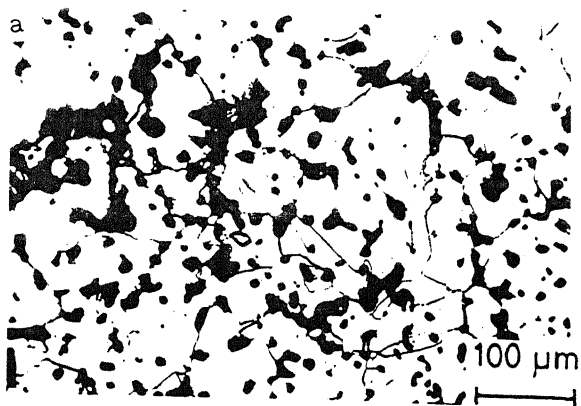
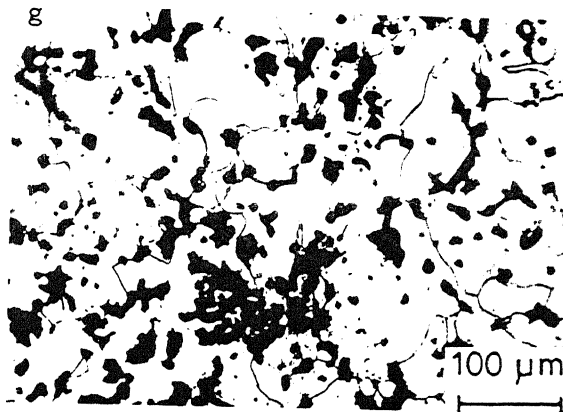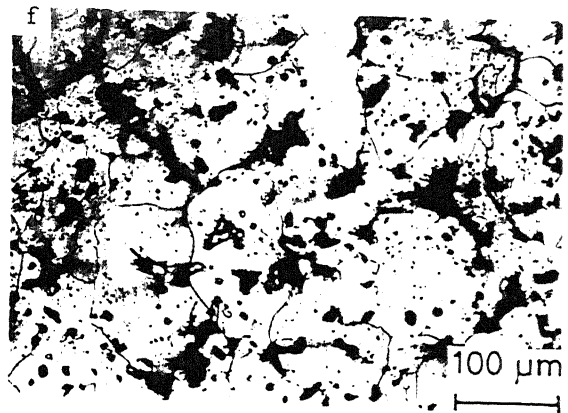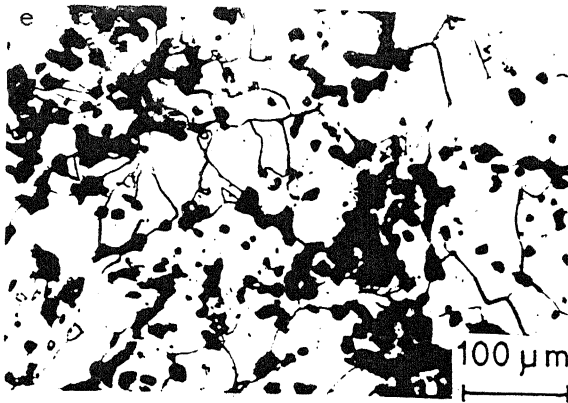Figure 3.5   Microstructures Of Steels (1.2% C) Containing
0-2% Manganese Or Chromium (Sintered At 1350°C For One Hour In
Dry Hydrogen)
     (a)   0% alloying ; (b) 0.5% Mn ; (c) 1.0% Mn ; (d) 2.0% Mn
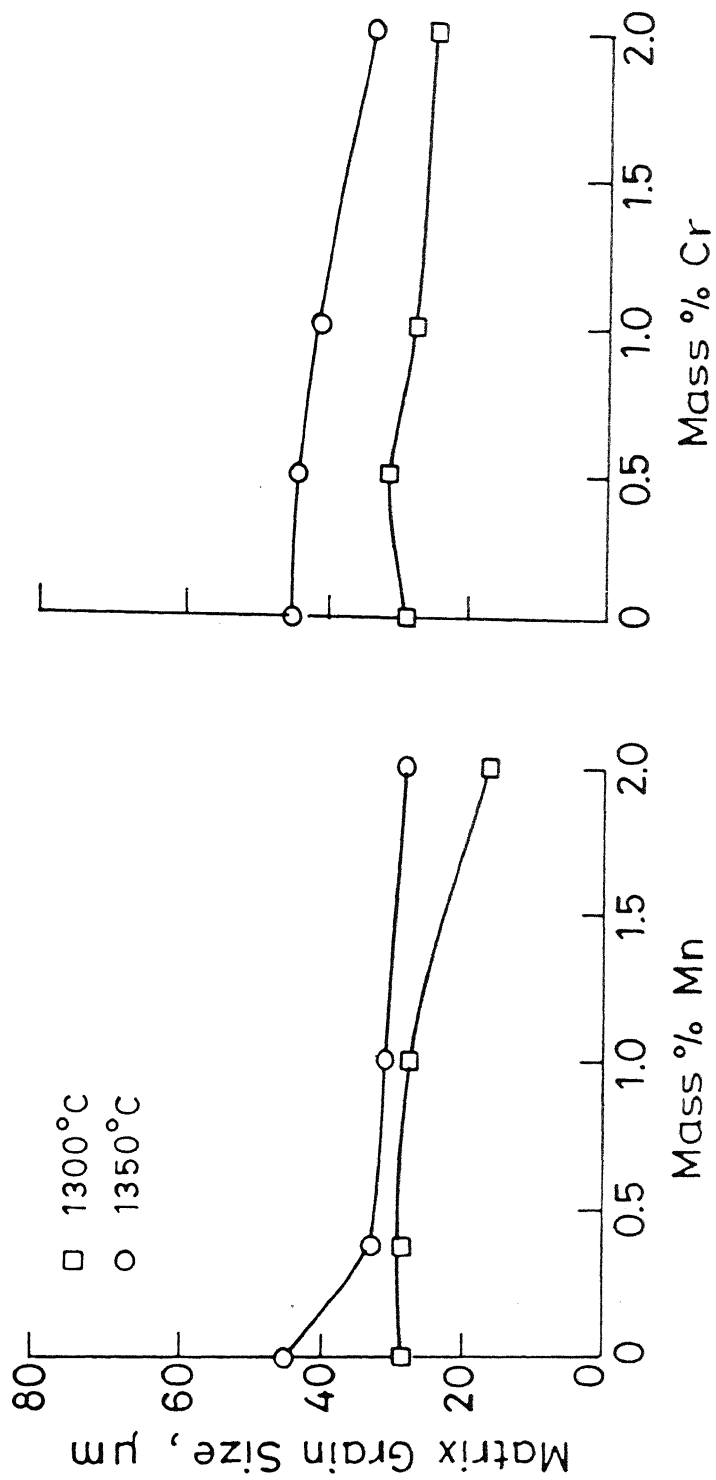   (e)   0.5% Cr ; (f) 1.0% Cr ; (g) 2.0% Cr

Figure 3.6   Matrix Grain Size Variation With Respect To Manganese Or Chromium Content For Steels Containing 1.2% C (Sintered at 1300°C – 1350°C For One Hour In Dry Hydrogen)

in the ferrite grain was present, such that at the grain boundary of the matrix phase, the concentration was invariably maximum [Table III.2] . However, in case of ferro-chromium addition, such a feature was not present. Undissolved ferro-chromium particles were more prevalent than the ferro-manganese particles [Figure 3.10].

III.3 1.2% C Steels with Mn and Cr addition

III.3.1 Sintered Density / Porosity

Figures 3.7 (a,b) show sintered density and porosity variations of 1.2% C steels with both manganese and chromium additions at three different sintering temperatures. From the plot, it is evident that the porosity variation of such steels is similar to that for chromium steels. The sintered porosity after 1350°C sintering exhibits lowest values. However, in the present case, the initial addition of chromium and manganese upto 0.5 wt % drastically reduced the sintered porosity.

III.3.2 Microhardness

From figure 3.7 (c), the microhardness variation reveals that at relatively higher alloying additions, i.e., greater than 0.5%, the values are higher than those for either manganese or chromium containing steels.

III.3.3 Compressive Yield Strength

0.2% offset yield strength values of steels containing both manganese and chromium after sintering at 1250°, 1300° and 1350°C are plotted in Figure 3.7 (d). In initial stage of alloying, i.e., upto 0.5%, the compressive strength values are

TABLE III.2

EDAX Analysis of Manganese or Chromium in 1.2% C Steels

Sintered at 1350°C

Location in Photo-Micrograph	Mn - Steel			Cr - Steel		
	0.5%Mn	1.0%Mn	2.0%Mn	0.5%Cr	1.0%Cr	2.0%Cr
A	0.58	1.21	1.07	0.74	1.47	2.75
B	0.63	1.18	1.12	0.77	1.56	2.53
C	0.44	1.46	1.93	0.65	1.27	2.73

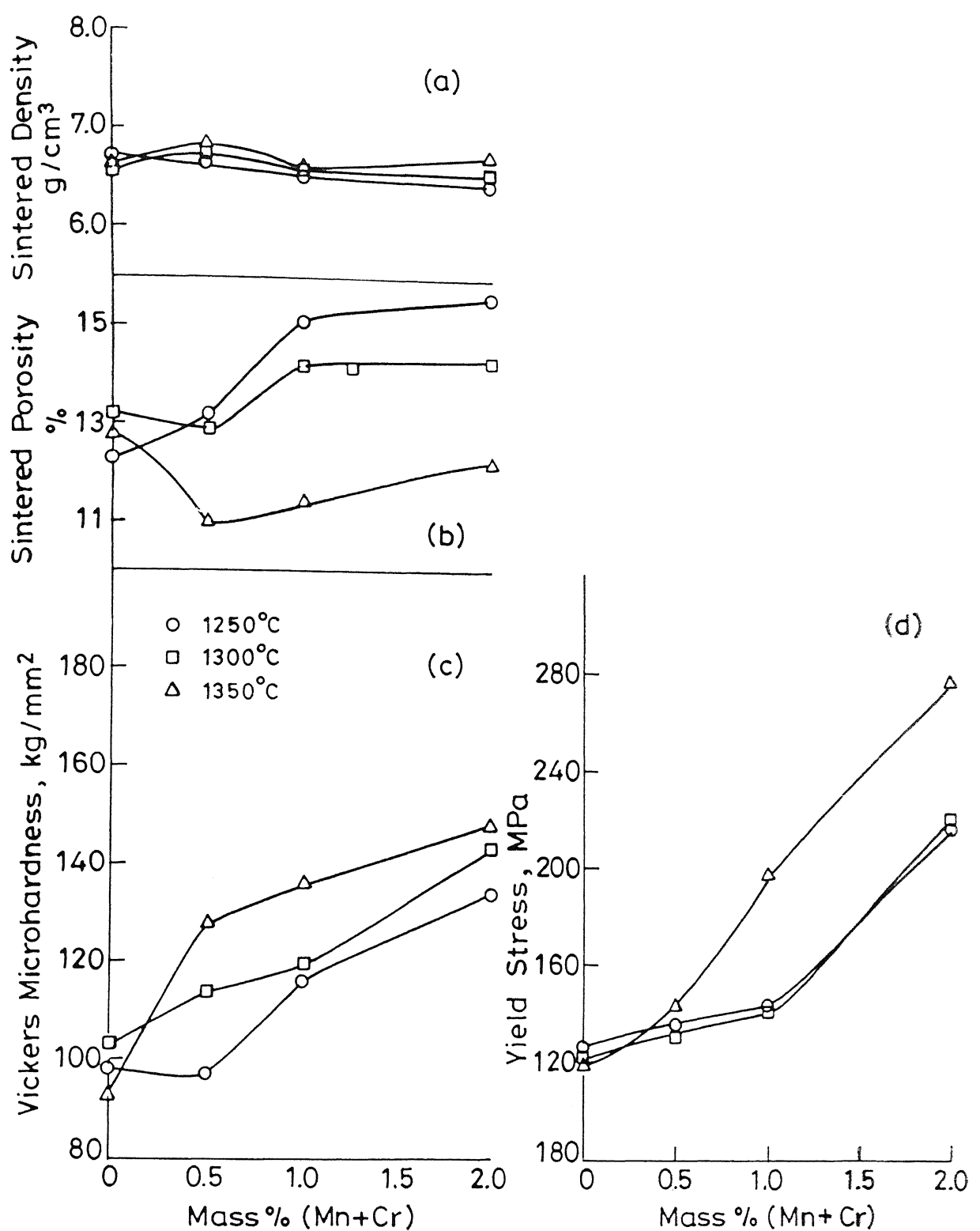A : Grain interior ; B : Near grain boundary ; C : At grain boundary

Figure 3.7 Sintered Properties Variations With Respect To Manganese And Chromium Contents For Steels Containing 1.2% C (Sintered At 1250°C – 1350°C For One Hour In Dry Hydrogen)

similar to straight manganese or chromium steels, but at higher contents of combined alloying when sintered at 1350°C, there is a significant increase in strength value (280 MPa).

III.3.4 Optical Metallography

The micro-structure of 1.2% C steels with manganese and chromium contents ranging from 0.5 to 2 wt % are given in Figures 3.8 (a-c). The micro-structures show mostly pearlitic stucture with some ferrite region.

III.3.5 SEM Studies

EDAX analysis of steels containing both manganese and chromium indicated no regular trend (Table III.3), similar to those containing straight ferro-chrome addition. This result is in contrast to steels containing only ferro-manganese additive.

III.4 Microstructure and Properties of Heat Treated Steels

The quenched hardness as compared to sintered hardness of 1.2% C steels can be seen from figure 3.12. The manganese steels gave higher hardness values than corresponding chromium containing ones after quenching. The resultant microstructure after quenching was a mixture of martensite, bainite and retained austenite.

In manganese - chromium steels similar structures were noticed with a slightly higher level of hardness.
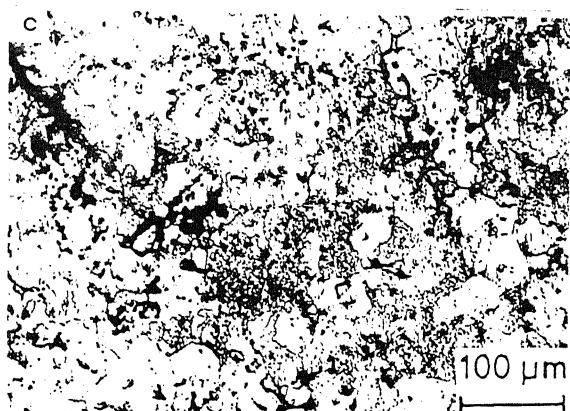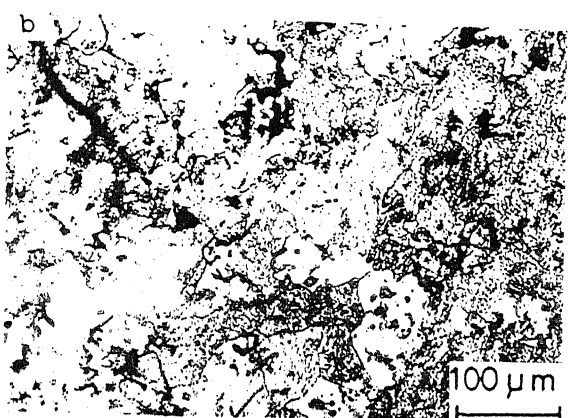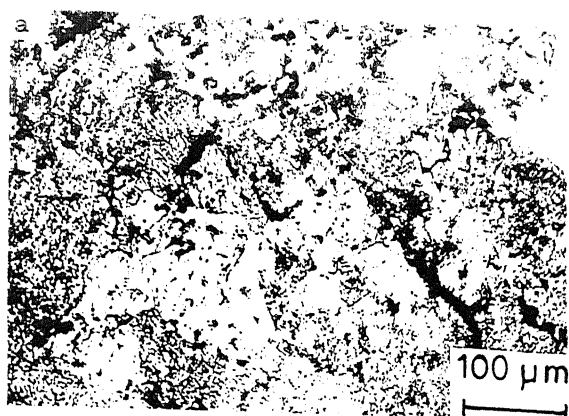
Figure 3.8   Microstructures Of Steels (1.2% C) Containing
Different Contents Of Manganese And Chromium (Sintered At 1350°C
For One Hour In Dry Hydrogen)
      (a)   0.5% Mn-Cr : (b) 1.0% Mn-Cr : (c) 2.0% Mn-Cr

TABLE III.3

EDAX Analysis of Manganese and Chromium in Mn-Cr Steels (1.2% C)

| Temp. | Location in Photo-Micrograph | Composition | | | | | |
		0.5 Mn-Cr Steel		1.0 Mn-Cr Steel		2.0 Mn-Cr Steel	
		Mn	Cr	Mn	Cr	Mn	Cr
1250°C	A	0.18	0.11	0.25	0.91	1.83	0.30
	B	0.14	0.09	0.38	0.69	1.91	0.27
	C	0.19	0.09	0.40	0.34	2.18	0.19
		Mn	Cr	Mn	Cr	Mn	Cr
1300°C	A	0.31	0.19	0.31	0.10	1.25	0.39
	B	0.20	0.19	0.29	0.13	1.38	0.23
	C	0.15	0.08	0.41	0.08	0.93	0.22
		Mn	Cr	Mn	Cr	Mn	Cr
1350°C	A	0.80	0.21	0.75	0.34	0.68	0.49
	B	0.61	0.23	0.68	0.42	0.83	0.48
	C	0.82	0.53	0.62	0.41	0.69	0.42

A : Grain interior ;   B : Near grain boundary ; C : At grain boundary
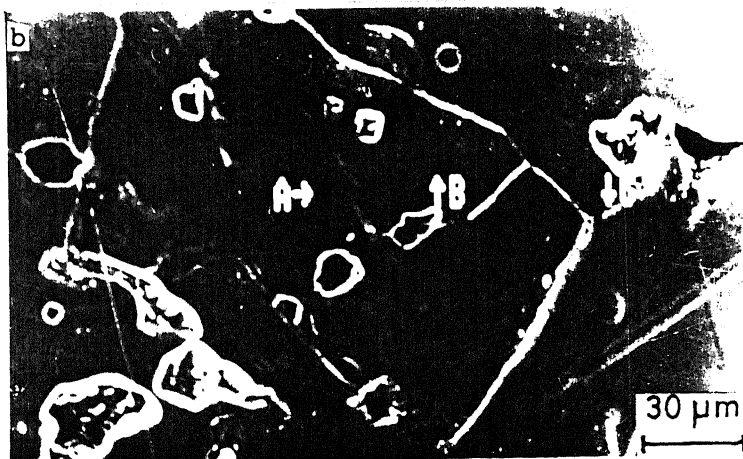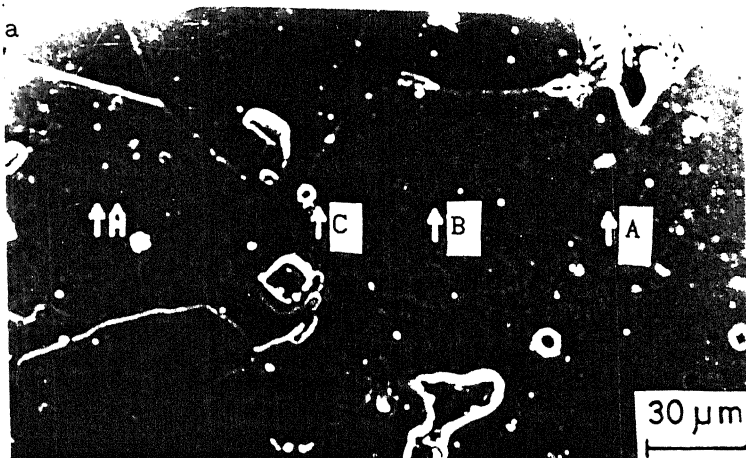
Figure 3.9 SEM Pictures Of 0.6% C Steels (Sintered At 1300°C For One Hour In Dry Hydrogen) Containing
(a) 1.0% Mn ; (b) 1.0% Cr
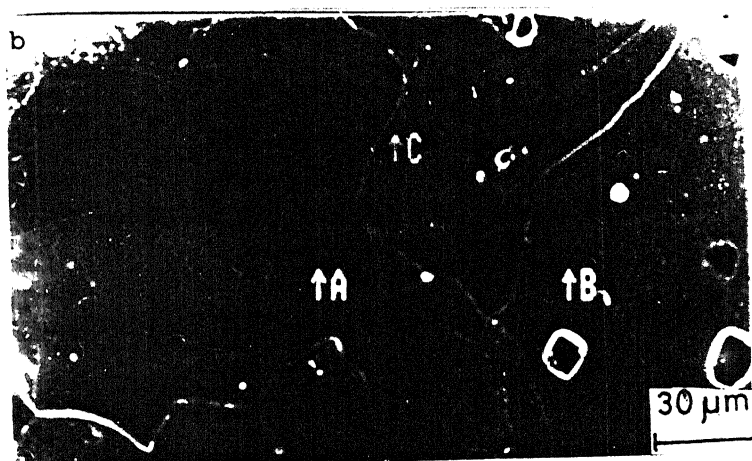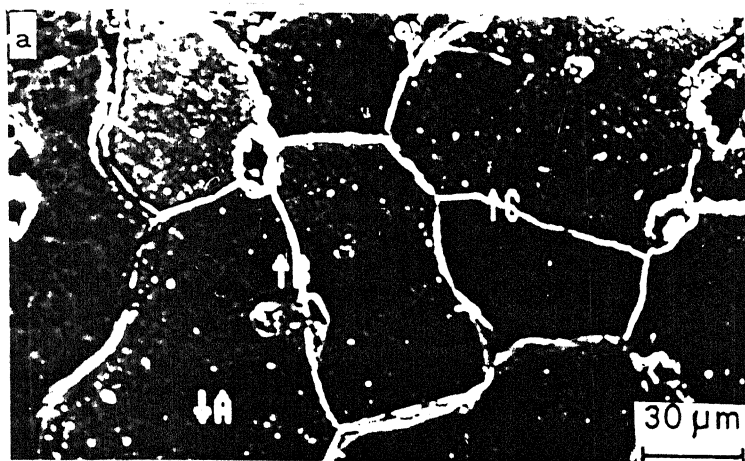
Figure 3.10   SEM Pictures Of 1.2% C Steels   'Sintered At
1350°C For One Hour In Dry Hydrogen) Containing
        (a)   2.0% Mn ; (b) 2.0% Cr
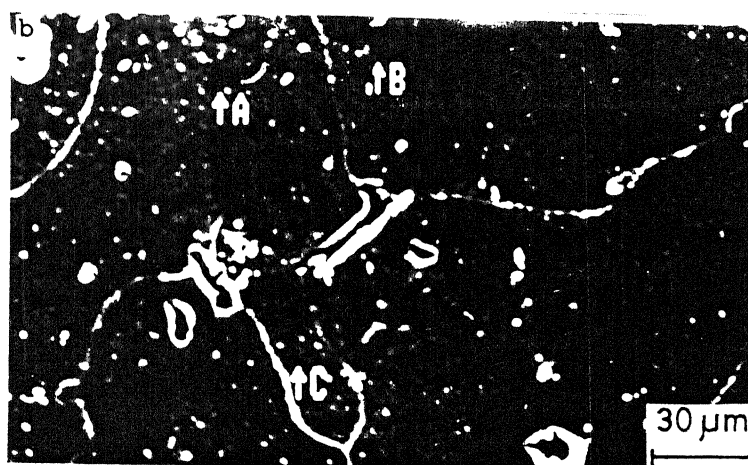
Figure 3.11 SEM Pictures Of 1.2% C Steels Containing Different Amounts Of Mn And Cr (Sintered At 1300°C For One Hour In Dry Hydrogen)
(a)   0.5% Mn-Cr ; (b) 1.0% Mn-Cr ; (c) 2.0% Mn-Cr
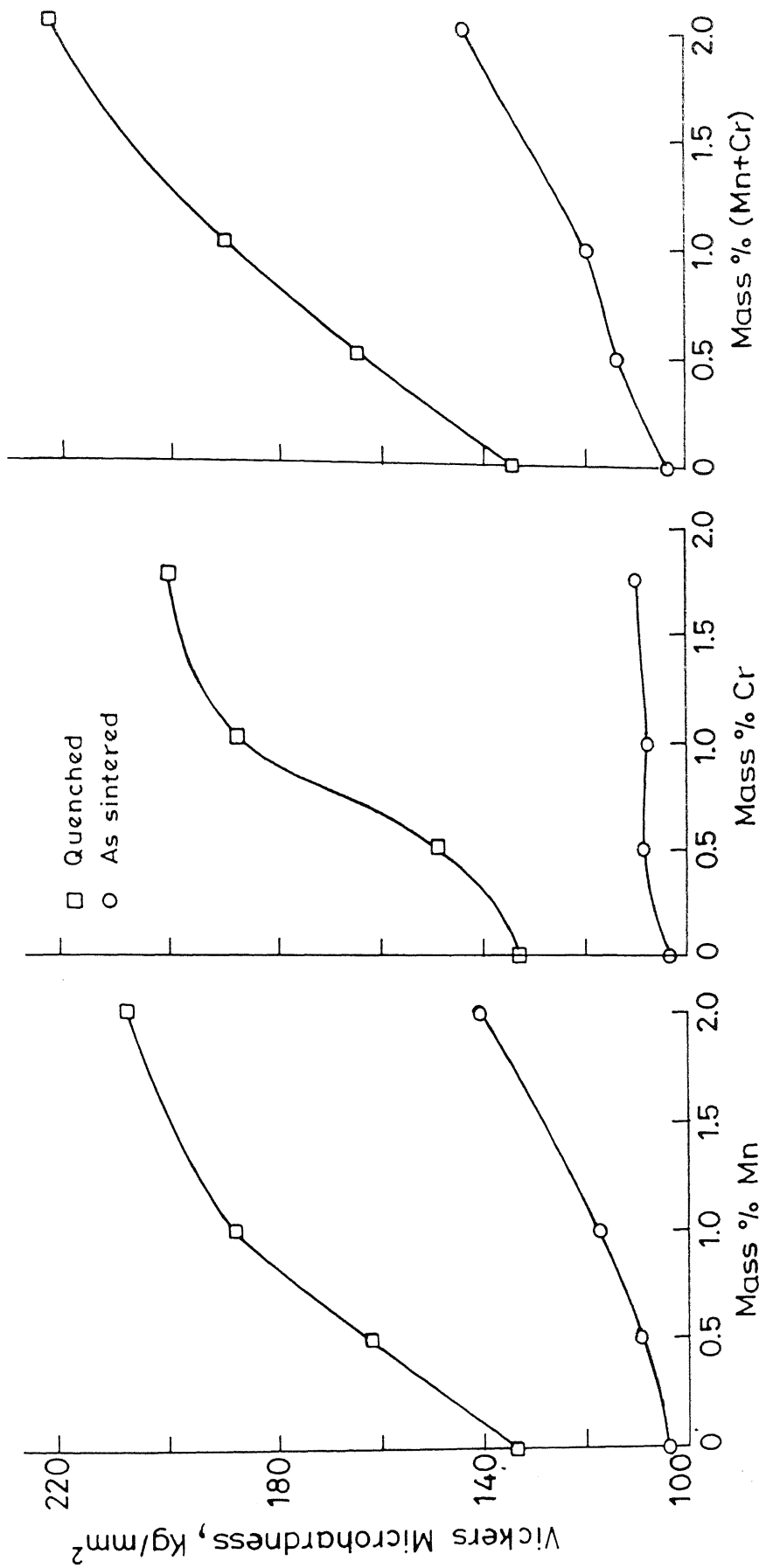
Figure 3.12 Vicker's Microhardness Variation Of 1.2% C Steels
Containing Mn, Cr, and Mn/Cr In Sintered And Heat Treated
Conditions (Sintering Temperature 1300°C)

CHAPTER IV

DISCUSSION

For developing high mechanical strength with satisfactory hardenability, the role of manganese and chromium as alloying addition is well established. In the present investigation, the alloying route was through ferroalloy, as these are cheap and easily available. Moreover, as these alloying additions are very much prone to oxidation, their addition as ferroalloy would lower their sensitivity towards that. In addition, as ferroalloys have lower melting points than the parent alloying element, e.g., manganese, chromium etc., the possibility of liquid phase sintering for densification could be very well exploited. The liquid phase is, of course, transient in nature because the constituents of the master alloy particles diffuse into the iron matrix.

IV.1   Effect of Ferroalloy Content

Densification : The high carbon (7.1% C) ferromanganese used in the present investigation gives rise to liquid phase at 1100°C [11]. An increased amount of liquid can, therefore, be expected with increase in the amount of ferromanganese addition. On the other hand as the melting point of low carbon ferrochrome used in the present study would be much higher (>1650°C) [27], the full exploitation of liquid phase sintering in such types of steels is ruled out. Densification is, therefore, poorer in chromium steels as compared to manganese ones. Moreover, sintered porosity values increase with increasing chromium content in the steels. From figure 3.7, it is evident that sintered porosity variations of manganese - chromium steels

were nearer in values to those of chromium steels. Unlike the effect of sintering temperature in the present case the initial addition of manganese and chromium upto 0.5 wt% drastically reduces he sintered porosity values. It is interesting that the sintered porosity values in such steels were similar to those of straight chromium containing steels, although in the former there was some presence of liquid phase as a result of high carbon ferromanganese addition. This suggests that any positive trend in densification by ferromanganese addition is anulled by equivalent addition of ferrochromium.

The EDAX analysis of steels containing manganese, chromium or a combination of both showed (Table 3.1 [a,b] and Table 3.3) that there was better material transport in manganese steels as compared to manganese-chromium steels.

<u>Mechanical Properties</u> : The mechanical properties of P/M steels are commensurate to densification and alloying distribution. In the present investigation, both microhardness and compressive yield strength values increased with increasing manganese content in manganese steels, while these values were lower for chromium steels. It appears that the effect of densification on hardness is prevalent such that the subtle differences in the intrinsic properties of respective carbides, i.e., chromium and manganese carbide, is not distinguishable. The EDAX analysis of steels (Table 3.1 [a,b]) shows that the amount of chromium dissolved in the Cr-steel matrix is less than theamount of manganese in manganese steels. This is obvious because chromium is a good carbide forming element and thus does not contribute to matrix solid solution hardening. The higher compressive yield strength of manganese steel (0.6% C) than the

corresponding chromium steel can be explained on the basis of grain size (Figure 3.3) which is smaller for the former at any sintering temperature.

In manganese-chromium steels except upto the initial stage of alloying, i.e., upto 0.5%, when compressive strength values were similar to straight manganese or chromium steels, there was a significant increase in strength with increase in the alloying addition. The microhardness variation of such steels also reveals that at relatively higher alloying addition, i.e., greater than 0.5 wt%, the values were higher than those for either manganese or chromium containing steels. This could be attributed to better densification at higher temperature, i.e., $1350^{\circ}C$, and to solid solution strengthening imparted by inter diffusion between manganese and chromium.

IV.2   Effect of Sintering Temperature

For manganese steels, in general, the sintered porosity is decreased as one goes for higher sintering temperature. This is attributed to greater amount of liquid phase formation at higher sintering temperatures. Though chromium has a better solid state diffusivity in iron (10.4×10^{-10} cm^2/s at $1250^{\circ}C$) [26] than manganese (1.7×10^{-10} cm^2/s at $1250^{\circ}C$) [26], a higher densification for manganese steels is noticed after sintering at $1350^{\circ}C$. This is due to the fact that all the ferromanganese added presently is transformed into liquid phase at $1316^{\circ}C$ [27]. For chromium steels also with increase in sintering temperature, there was a general decrease in porosity level. This is because of better diffusivity at higher sintering temperature [26]. However, a direct comparison with similar manganese containing steel is not possible because the latter

with high carbon ferromanganese additive undergoes complete liquid phase transformation and thus appreciably enhances diffusivity. This is the reason of manganese steels showing higher hardness and compressive yield strength values after high temperature sintering (1350°C).

The EDAX analysis carried out in SEM reveals (Table 3.1 [a,b]) that at elevated temperature sintering (1300°C) the amount of manganese dissolved in the matrix is lower than that at 1250°C sintering. This suggests that during sintering at elevated temperature, carbon added as premix diffuses so as to get dissolved into the ferrous matrix and also to form respective carbides depending on carbide forming additives. Among Cr_7C_3 and Mn_7C_3 the free energy of formation for the former is lower (-204.3 kJ/mol) [26] than the latter (-113.9 kJ/mol) [26], hence confirmimg the better stability of chromium carbide than manganese carbide. This can be seen from EDAX analysis result (Table 3.4 [a,b]) where the amount of dissolved chromium is less than that of manganese in the matrix.

The sintered porosity of manganese chromium steels at 1350°C naturally exhibited lowest values because of the obvious reason, i.e., higher fraction of liquid phase formation and better inter-diffusion of alloying element. This also attributes to higher hardness and compressive yield strength when sintered at 1350°C as compared to relatively lower temperature sintering.

IV.3   Effect of Carbon Content

In manganese containing steels with an increase in carbon content from 0.6 to 1.2%, there was a general decrease in sintered porosity level. Since manganese is not a good carbide

former, the added extra carbon straight away contributes to liquid phase densification. In chromium containing steels, with increase in the carbon content, there was not much change in sintered porosity level. Even carbon addition as much as 1.2% is not enough for liquid phase sintering. It may be possible that chromium interacts faster with carbon to form carbide and thus not enriching the ferrous matrix by carbon. At the same time the grain size of chromium steels reduced drastically with the increase of the carbon content, the effect of which is reflected as higher yield strengths (Figure 3.4) for chromium steels with 1.2% C. The data reveal that with increase in the amount of alloying element in 1.2% C steels microhardness increases uniformly showing a greater effect in manganese containing steels as compared to chromium containing ones. The higher microhardness values of ferrous matrix for manganese containing steels as compared to chromium steels can be attributed to more dissolution of carbon in the former giving rise to solid solution hardening. The role of sintering temperature in case of high carbon containing steels is to encourage more amount of carbide formation. This is the reason why the microhardness of the matrix is lowest in the highest sintering temperature, i.e., 1350°C.

IV.4   Heat Treatment Response of Sintered Steels

It was noticed that manganese is more effective than chromium in hardening sintered low alloy steels (Figure 3.2) after quenching treatment. This can be supported by the multiplying factor described in Chapter I (Figure 1.1) [1]. Another reason why the full exploitation of hardening in chromium steels is not possible is the presence of undissolved chromium carbides at the selected austenitizing temperature, i.e., 870°C.

The hardness values of manganese - chromium
steels after quenching are more than those of either manganese or
chromium steels (Figure 3.12). This is because of the synergistic
effect of alloying additions [28].

CHAPTER V

CONCLUSIONS

The various inferences drawn on the basis of this investigation are enumerated below.

(1) Among manganese and chromium as alloying addition, former imparts better densification to sintered steels. This is attributed to the fact that the former system undergoes liquid phase sintering.

(2) In spite of chromium having higher diffusivity in iron than manganese, homogeneous distribution of alloying addition is better in the latter case.

(3) Manganese contributes better than chromium towards strengthening the sintered low alloy steels.

(4) A combination of manganese and chromium is better than either manganese or chromium addition for enhancing the mechanical properties of sintered low alloy steels.

(5) High temperature sintering (1350°C) is advantageous in developing P/M steels containing oxidation prone alloying elements, e.g., manganese and chromium.

(6) The effect of increasing carbon content from 0.6 to 1.2% in enhancing the strength is more in case of chromium steels than in manganese steels.

(7) As dissolution of chromium carbide needs much higher temperature than the selected austenitizing temperature (870°C), the full exploitation of hardening in chromium steels is not possible.

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